TREATISE ON GENERAL AND INDUSTRIAL ORGANIC CHEMISTRY

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PART II

WITH 303 ILLUSTRATIONS

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(Oils, Fats, Waxes, Candles, Soaps)

The compounds or *esters* formed by alcohols with inorganic acids have already been studied (*see* pp. 234 *et seq.*), and we shall now consider the esters resulting from the substitution of the typical hydrogen of organic acids by alkyl radicals. Various isomerides exist with these compounds, *e.g.*, methyl butyrate is isomeric with ethyl propionate, butyl formate with propyl acetate. Attention will, however, be paid more especially to the esters of glycerine (*glycerides*), since on these are based the fat, oil, soap, and candle industries.

PREPARATION. These esters may be obtained by the general methods already described (*loc. cit.*), *e.g.*, by the action of the acid chlorides or anhydrides on the alcohols or sodium alkoxides :

$$C_2H_5 \cdot CO \cdot Cl + C_2H_5 \cdot OH = HCl + C_2H_5 \cdot COOC_2H_5.$$

They are formed also by the interaction of the silver salt of the acid and the alkyl iodide, and by the action of gaseous hydrogen chloride on a hot alcoholic solution of the nitrile of the acid. Further, the alcohols and acids themselves react, slowly in the cold and more rapidly although not completely in the hot, with formation of esters :

$$C_2H_5 \cdot OH + CH_3 \cdot CO_2H = CH_3 \cdot CO_2C_2H_5 + H_2O.$$

In practice the preparation is carried out as follows : the dry organic acid is mixed with an excess of absolute alcohol and the mixture saturated with dry hydrogen chloride gas, left for some time in a moderately warm place and then poured into water ; the ester separates in an insoluble form after neutralisation of the aqueous liquid with alkali in the cold.

In this reaction the acid chloride is probably formed as an intermediate product : $CH_3 \cdot CO_2H + HCl = H_2O + CH_3 \cdot CO \cdot Cl$; the latter—which with water might give the reverse reaction—being in presence of excess of the alcohol, forms the ester (equation given above). Esterification is, however, never complete, as the reaction is a reversible one, the hydrochloric acid and also other inorganic acids such as sulphuric acid, even in the dilute state, behaving as true *moist catalysts* (Berthelot, 1879 ; V. Meyer, Fischer and Speier, 1895 ; Senderens and Aboulenc, Sabatier and Mailhe, 1909–1913) :

$$C_nH_{2n+1} \cdot OH + C_nH_{2n}O_2 \rightleftarrows H_2O + C_nH_{2n-1}O_2 \cdot C_nH_{2n+1}.$$

After a certain time a system is obtained which contains given quantities of alcohol (a), acid (b), water and ester (z). The same equilibrium is attained by mixing 1 mol. of ester and 1 mol. of water as by mixing 1 mol. of acid and 1 mol. of alcohol, and this equilibrium is represented by the following equation for bimolecular reactions (*see* Vol. I., p. 69) : $k(a-z)(b-z) = k_1z^2$, where a and b represent the respective initial concentrations of alcohol and ester and z that of the ester and water when equilibrium is reached, all expressed in *mols.* (gram-molecules) ; k and k_1 are constants depending on the nature of the reaction and, according to a definite law, slightly on the temperature. If, for convenience, $\frac{k_1}{k}$ is made equal to K, the equation becomes : $(a-z)(b-z) = Kz^2$.

With 46 grams of alcohol and 60 grams of acetic acid (gram-molecules), it is found experimentally that $K = 0{\cdot}25$, and, as a and b both assume the value 1, 1 mol. of each reacting, the equation becomes $(1 - z)^2 = 0{\cdot}25\,z^2$, *i.e.*, $1 - z = 0{\cdot}5\,z$ or $z = \frac{2}{3}$. This means that when a state of equilibrium is reached, the system contains $\frac{1}{3}$ mol. of acetic acid + $\frac{1}{3}$ mol. of alcohol + $\frac{2}{3}$ mol. of ester + $\frac{2}{3}$ mol. of water. Every substance participating in the equilibrium acts in proportion to its mass. If the above equation is given the form $\frac{a - z}{z} = K\frac{z}{b - z}$, it becomes evident that, in order to displace the equilibrium so as to have a greater value of z (*i.e.*, of esterification), the value of a must be increased and that of b decreased, esterification being complete when $a = \infty$. The same final result is obtained when b is much greater than a, esterification again being complete when $b = \infty$. In practice, almost complete esterification is attained when 1 mol. of acid is employed per 10 mols. of alcohol or *vice versa*. That the same result is obtained with excess of alcohol as with excess of acid is shown by the above equation, since, if instead of m mols. of both acid and alcohol, n times as many molecules of acid are taken, the equation becomes: $\frac{m - z}{z} = K\frac{z}{n \cdot m - z}$; whilst if n times as many molecules of alcohol are taken, it becomes: $\frac{n \cdot m - z}{z} = K\frac{z}{m - z}$. These two equations are identical, multiplication of the terms of the former by $\frac{n \cdot m - z}{m - z}$ giving the latter.

The limit of esterification is modified but slightly by change of temperature, and amounts, in the case of acetic acid, to 62·2 per cent. at 10° and to 66·5 per cent. at 220°.

Sabatier and Mailhe (1909–1913) have shown that in many cases esters are obtained with dry *catalysts*, especially thorium oxide or, better, titanium oxide at about 300°; over these is passed the mixed acid and alcohol vapours in suitable proportions, *i.e.*, with excess of one or the other component. When, however, a certain temperature, varying with the nature of the catalysing oxide, is exceeded the reaction becomes reversible and more or less decomposition occurs.

The esters of monohydric alcohols and monobasic fatty acids are neutral liquids lighter than water (0·8 to 0·9) and pleasant smelling (some forming artificial fruit essences); they are slightly soluble in water (the first members more soluble than the higher ones) and they boil undecomposed.

By means of Grignard's reaction (*see* p. 243) they yield tertiary alcohols.

The esters are hydrolysed into their components when heated with alkali, mineral acid, or aluminium chloride, or superheated with water. The mineral acid has a purely catalytic accelerating action on the following reaction due to the water, which is very slow in its action:

$$CH_3 \cdot CO_2C_2H_5 + H_2O = C_2H_5 \cdot OH + CH_3 \cdot CO_2H.$$

With bases, the hydrolysis is expressed by the equation:

$$CH_3 \cdot CO_2C_2H_5 + NaOH = C_2H_5 \cdot OH + CH_3 \cdot CO_2Na.$$

The hydrolysing velocity of acids and bases depends on their degrees of dissociation, *i.e.*, on their strengths, so that feeble acids and bases hydrolyse far more slowly than the strong ones. In the case of acids, the hydrolysis is caused by the hydrogen ions, and in that of bases by the hydroxyl ions. In the latter instance, however, the velocity of hydrolysis is greater than with acids, and with methyl acetate, the value of K for decinormal potassium hydroxide is 1350 times that for decinormal hydrochloric acid. In the hydrolysis of fats, the acids of which are feeble and the resultant salts therefore hydrolytically dissociated to a marked extent (*i.e.*, even with excess of fatty acid, there always remains free base or hydroxyl ions), complete hydrolysis is obtained industrially with a quantity of base (*e.g.*, lime) much less than that required theoretically.

As has been already mentioned, the esters of the first monobasic acids and monohydric alcohols are, in general, substances of pleasing odour and are used with suitable admixtures as artificial fruit essences.[1]

ETHYL FORMATE, $H \cdot COOC_2H_5$, boils at 55° and is used for artificial *rum* or *arrack*.

METHYL ACETATE, sp. gr. 0·9577, b. pt. 57·5°, is used to dissolve cellulose to make the varnish ("dope") for aeroplanes; in its manufacture from acetates, sulphuric acid and methyl alcohol, the plant is rapidly attacked, even if enamelled. Duchemin obtains the ester directly from pyroligneous acetic acid and methyl alcohol by means of a catalyst (the nature of which is not disclosed), a yield of 95 per cent. being thus obtained and the intermediate preparation of calcium acetate avoided; the resulting ester is then rectified (*see also* Ger. Pats. 232,818, 277,111, 277,187, 277,188, 285,990, and 286,812).

ETHYL ACETATE or Acetic Ester, $CH_3 \cdot COOC_2H_5$, is used in medicine and for the preparation of ethyl acetoacetate, which is of considerable importance in organic syntheses. It is prepared by heating alcohol with acetic and sulphuric acids under the conditions given above. It boils at 77° and has the sp. gr. 0·9238 at 0°.

AMYL ACETATE, $CH_3 \cdot COOC_5H_{11}$, has the sp. gr. 0·8762 at 15° and b. pt. 138° to 139°, and forms a colourless, fairly mobile inflammable liquid, of neutral reaction and with the odour of pears; it is very highly soluble in alcohol or ether and slightly so in water, and burns with a luminous flame. It is used as a solvent for cellulose acetate and celluloid in the preparation of varnishes, especially aeroplane "dope"; to some extent it serves for making alcoholic solutions of artificial fruit (pear) essences.

The crude impure product is prepared directly from fusel oil (*see* p. 165) and acetic and sulphuric acids (calcium acetate is also used). The pure ester is obtained by heating 100 parts of pure amyl alcohol, 100 of glacial acetic acid, and 50 of concentrated sulphuric acid for two to three hours at 100° in a copper vessel fitted with a reflux condenser. It is then distilled in a current of steam, the vapours being rectified slightly by means of a short column. The distillate is washed with a little sodium bicarbonate solution and twice with a little water, and is then dried by means of fused calcium chloride. The final product contains 85 to 95 per cent. of amyl acetate, the rest being amyl alcohol. The yield is about 95 per cent., the loss of sulphuric acid amounting to 6 per cent. A second rectification yields a purer product. Amyl acetate may be obtained also by passing amyl alcohol and acetic acid vapours over a catalyst, *e.g.*, dry titanium oxide at 280° to 290° (or oxide of thorium or glucinum). Prior to the war the commercial product cost £5 to £6 per cwt., and the pure ester about double as much.

[1] Commercial *fruit essences* are prepared from the following mixtures of esters, and formerly cost from 2*s.* 6*d.* to 5*s.* per kilo:

Essence of pineapple: 25 grams ethyl butyrate + 135 grams amyl valerate + 5 grams chloroform + 5 grams aldehyde + 850 grams alcohol.

Essence of apples: 50 grams ethyl nitrite + 50 grams ethyl acetate + 100 grams amyl valerate + 40 grams glycerol + 7·5 grams aldehyde + 7·5 grams chloroform + 745 grams alcohol.

Essence of pears: 200 grams amyl acetate + 50 grams ethyl acetate + 100 grams ethyl nitrite + 20 grams glycerol + 630 grams alcohol.

Essence of apricots: 45 grams benzaldehyde + 190 grams amyl butyrate + 10 grams chloroform + 765 grams alcohol.

Essence of strawberries: 27 grams amyl acetate + 18 grams amyl valerate + 9 grams amyl butyrate + 9 grams amyl formate + 15 grams ethyl acetate + 7 grams essence of violets + 915 grams alcohol.

Essence of peaches: 100 grams amyl valerate + 100 grams amyl butyrate + 20 grams ethyl acetate + 10 grams benzaldehyde + 770 grams alcohol.

The natural essences of the citrus fruits were given on p. 415

The amounts of different volatile oils and essences imported into France were (tons): 845 in 1913, 612 in 1914, and 759 in 1915.

ETHYL BUTYRATE, $C_3H_7 \cdot COOC_2H_5$, boils at 121° and is used as essence of pineapple and in rum.

ISOAMYL ISOVALERATE, $C_4H_9 \cdot COOC_5H_{11}$, boils at 194° and is used in essence of apples.

The *higher esters* form constituents of waxes (**Cetyl Palmitate**, $C_{16}H_{31}O_2C_{16}H_{33}$; **Melissyl Palmitate**, $C_{16}H_{31}O_2C_{30}H_{61}$; **Ceryl Cerotate**, $C_{26}H_{51}O_2C_{26}H_{53}$, etc.). These higher esters distil unchanged only in a vacuum; under ordinary pressure they decompose into olefines and fatty acids.

Esters of Polybasic Acids are prepared by the general methods described above; acid esters are obtainable if one or more of the carboxyl groups are not esterified.

The esters of oxalic acid are obtained, for instance, by heating anhydrous oxalic acid with alcohols, the normal ester being separated from the acid ester by fractional distillation.

The importance of **Malonic Esters** in organic syntheses has already been illustrated on pp. 368 *et seq.;* the normal methyl ester boils at 181° and the ethyl at 198° (sp. gr. 1·068 at 18°). The two hydrogen atoms united with the middle carbon atom may also be replaced by alkyl groups. Thus, for example, **Ethyl Dimethylmalonate**, $(C_2H_5 \cdot CO_2)_2 : C(CH_3)_2$, is obtained from the sodium derivative by treatment with methyl iodide. These compounds, when heated, lose CO_2 and yield alkylacetic derivatives. Similar relations are found with the alkyl derivatives of succinic acid or esters.

The preparation of **Ethyl Acetoacetate** and its importance in organic syntheses have been dealt with on p. 396.

The **Normal Methyl Ester** of succinic acid, $CH_3 \cdot CO_2 \cdot CH_2 \cdot CH_2 \cdot CO_2 \cdot CH_3$, melts at 19° and boils at 80° under 10 mm. pressure; the *ethyl ester* boils at 216°.

GLYCERIDES, OILS, FATS

Glycerol being a trihydric alcohol, its three alcoholic groups may be partially or wholly esterified by acid residues. It suffices, indeed, to heat glycerol with fatty acids to obtain mono-, di-, and tri-glycerides. These glycerides are also formed by the action of the tissues of the pancreas on a mixture of oleic acid and glycerol, a still better method for synthesising fats being the treatment of the sulphuric ethers of glycerol with fatty acids dissolved in concentrated sulphuric acid. Most fats and oils are formed of triglycerides, which, according to the nature of the fatty acid saturating the three alcoholic groups of the glycerol, are termed **Tripalmitin** (melts at 60°), **Tristearin** (melts first at 55° and, after resolidification, at 71·6°), and **Triolein** (liquid, solidifying at about 0°).

Triolein, which is the principal component of liquid fats and especially of olive oil, is formed by the esterification of the glycerol molecule with 3 mols. of oleic acid (*see* p. 358):

$$\begin{array}{l} CH_2 \cdot O \cdot O \cdot C_{18}H_{33} \\ | \\ CH \cdot O \cdot O \cdot C_{18}H_{33} \\ | \\ CH_2 \cdot O \cdot O \cdot C_{18}H_{33}. \end{array}$$

Mono- and di-glycerides are not found in the fats (only ravison oil contains a diglyceride, *dicrucin; see also* esters of polyhydric alcohols and glycerol with mineral acids, pp. 356, 381 *et seq.*).

Certain fats (butter, cocoa-butter) contain mixed triglycerides, *i.e.*, with different acid radicles, some of them being of acids of low molecular weights, soluble in water.[1] A. Grun (1906–1909) synthesised mixed glycerides con-

[1] *Volatile fatty acids soluble in water.* The number of c.c. of decinormal potassium hydroxide solution required to neutralise the volatile fatty acids soluble in water from 5 grms. of the fat

taining three acid residues, all different.[1] The most simple glyceride is **Triformin**, $C_3H_5(CO_2H)_3$, which was obtained crystalline by P. van Romburgh (1910) by protracted heating of glycerol with 100 per cent. formic acid; it crystallises with difficulty, melts at 18°, boils at 266° (762 mm. pressure), and at 210°, under ordinary pressure, decomposes. It is hydrolysed slowly by cold, rapidly by hot water.

constitutes the so-called **Reichert-Meissl-Wollny number**, and serves to ascertain the purity of certain fats, especially of butter. The determination is made as follows: exactly 5 grms. of the fat (melted at a low temperature and rapidly filtered) is heated in a flask of about 350 c.c. capacity with 10 c.c. of alcoholic potash (20 grms. of KOH in 100 c.c. 70 per cent. alcohol) on a water-bath with frequent shaking until almost all the alcohol is evaporated; the remainder of the alcohol is completely expelled by shaking the flask and introducing a current of air every half-minute. After about twenty minutes, when the smell of alcohol is no longer detectable, 100 c.c. of distilled water is added, the heating being continued until a clear solution is obtained (if the liquid does not become clear the test must be commenced anew, hydrolysis being incomplete). To the tepid solution are then added 40 c.c. of the dilute sulphuric acid (1 vol. conc. H_2SO_4 + 10 vols. water) and a few fragments of pumice, the flask being then placed on a double wire-gauze and the liquid distilled, the dimensions of the apparatus being shown in mm. in Fig. 254. In about half an hour, exactly 110 c.c. of liquid distils over; this is mixed and filtered through a dry filter, 100 c.c. of the filtrate being titrated with decinormal KOH solution in presence of phenolphthalein. The volume of the alkali used is increased by one-tenth of its value (the volume of the distillate being 110 c.c.) and diminished by the number of c.c. of the alkali obtained from a control experiment made without fat as a check on the reagents employed. The result is the Reichert-Meissl-Wollny number. At the present time many laboratories employ the Leffmann-Beam-Polenske method, which effects more rapid hydrolysis (*see later*, Butter). For butter the limits for this number allowed by law are 26 to 31·5 (Municipal Laboratory of Milan), the butter being suspected if it gives a value of 22 to 26, although the butter of certain districts and from certain animals may, in exceptional cases, give a number as low as 21. The value for rancid butter, even two months old, is only slightly lower (by about 2) than the normal.

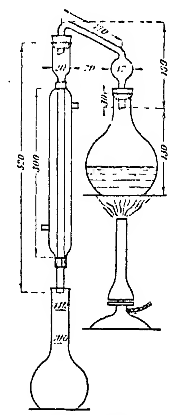

FIG. 254.

Insoluble fatty acids. The quantity of fatty acid insoluble in water obtainable from 100 parts of fat is called the **Hehner number**, and is determined as follows: into a flask of about 200 c.c. capacity is dropped, from a weighed vessel containing the dry filtered fat, 3 to 4 grms. of the substance, the vessel being then reweighed exactly. After addition of 50 c.c. of alcohol and 1 to 2 grms. of KOH, the flask is heated on a water-bath for five minutes, a clear solution being obtained. If the addition of a drop of water produces turbidity, saponification is incomplete, and the heating is continued for a further period of five minutes, the liquid being then tested as before. Evaporation is then continued until there remains a dense mass, which is taken up in 100 to 150 c.c. of water, acidified with dilute sulphuric acid, and heated until the clear fatty acids float on the surface. The liquid is then poured on a dry, tared filter (about 12 cm. in diameter and in a funnel either without a neck or with a very short one), previously half filled with hot water. The acids are washed with boiling water until the washing water ceases to show an acid reaction (as much as 2 litres of water is sometimes required). The filter is then cooled in a beaker of water so that the fatty acids solidify. The filter is then detached from the filter and introduced, with the acids, into a tared beaker, which is heated in an oven at 100° to 102° until its weight remains almost constant (difference between two weighings less than 1 mgrm.). The weight of fatty acids, referred to 100 parts of fat, represents the Hehner number.

Unadulterated fats generally have Hehner numbers of 95 to 97 (for butter it is 87·5; for coconut oil, 85 to 92; for palm-kernel oil, 91).

[1] The synthesis of triolein has been applied practically by G. Gianoli (1891) to diminish the rancidity of oils, especially of *olive oil* obtained from the pressed residue by means of carbon disulphide. This oil contains 20 to 30 per cent., or even more, of oleic acid, and is heated in an autoclave with the corresponding quantity of glycerol (or even a slight excess) at 250° in a slow stream of CO_2, or in a vacuum with a trace of oxalic acid to facilitate mixing of the liquids and avoid blackening of the mass owing to the presence of hydroxy-acids; the distillation of the water formed in the reaction is hastened by adding fragments of tin to the mass. This procedure yields a neutral or almost neutral oil with an iodine number less than 75 and a marked viscosity, so that it may be used even for mixing with lubricating oils. Bellucci (1911) also achieved an almost quantitative synthesis by heating together the theoretical proportions of glycerol (1 mol.) and fatty acid (3 mols.) at 180° to 260° for two hours in a vacuum, so as to expel the water formed, which would otherwise produce the reverse reaction; in a current of CO_2, the same reaction takes place at the ordinary pressure. A. Walter (1911) obtained a mixture of tri- and di-oleins by treating glycerol and acetic acid in presence of the enzymes of castor oil seeds, which act as catalysts. Indeed, *catalysts* cause reversible reactions, and while in presence of water the enzymes of castor oil seeds hydrolyse fats (*see later*, Biological Saponification) with formation of glycerol and fatty acids, if water is excluded as much as 35 per cent. of the fatty acids may be converted into glycerides.

Oils and fats have coefficients of expansion greater than those of other liquids (100 litres of olein at 0° becomes 101·6 at 20°).

Fats and, still more, waxes contain also non-glyceride components, *e.g.* **Cetyl Alcohol**, $C_{16}H_{34}O$, which, as such or as palmitic ester, forms one of the principal constituents of spermaceti fat. **Cerotic Acid**, $C_{27}H_{52}O_2$, and its ester occur in large proportions in wax. *Non-hydrolysable substances* (cholesterol, phytosterol, isocholesterol, aromatic alcohols, etc.) are always found in small quantities in fats (olive oil, about 0·75 per cent.; ravison oil, 1 per cent.; cottonseed oil, 1·6 per cent.; lard, 0·25 per cent.; cod liver oil, 0·5 to 3 per cent.; tallow, 0·02 to 0·6 per cent.; bone fat, 0·4 to 2·4 per cent.; wool fat more than 7 per cent.). The oils of cereals and of *Leguminoseæ* contain abundant amounts of **LECITHIN**, $C_{42}H_{86}O_9NP$, which is decomposed by the enzyme of the pancreas or castor oil seed, but not by that of the blood (*serum lipase*). The fat of peas contains 1·17 per cent. of phosphorus or 30·4 per cent. of lecithin, and that of wheat, 0·25 per cent. of phosphorus or 6·5 of lecithin. Lecithin abounds in the brain, nerves, blood corpuscles, and egg-yolk; for its constitution, *see* chapter on Proteins. The amount of lecithin is obtained by multiplying that of phosphorus by 26.

Fresh fats and oils contain minimum proportions of free fatty acids (less than 1 per cent.), these increasing with lapse of time, especially if the fats are not melted.

This rancidity is facilitated by sunlight and also by the protein substances of unrefined fats and oils. Coconut oil does not readily turn rancid, but with olive oil the proportion of free oleic acid reaches 25 per cent., and with palm oil as much as 70 per cent. of free acids may be formed. The *taste* and *smell* of fats depend, not on the glycerides, but on other substances.

The *specific gravity* of oils and fats varies from 0·875 to 0·970 (*see* Table given later) and is determined by means of an aerometer or Westphal balance (*see* Vol. I., p. 76). They are almost completely insoluble in water, acetone, or cold alcohol (this dissolves a certain amount of castor oil and of olive-kernel oil). The solubility increases markedly in boiling alcohol and is complete in ether, chloroform, carbon disulphide or tetrachloride, petroleum or petroleum ether (in the last two, castor oil is slightly soluble, while ether dissolves a little *pure* tristearin).[1]

When heated on a spatula held some distance above a flame, all fats give greenish flames, owing to the presence of carbon monoxide and sodium; also all fats are blackened by osmium tetroxide (sensitive reaction).

Oils dissolve small quantities of sulphur or phosphorus and larger quantities of soaps even when they are dissolved in ether or petroleum ether.

The oxygen of the air exerts a marked and rapid influence, as it is fixed by the *drying oils* (linseed, walnut, hempseed, poppyseed, etc.), which are thus transformed into *varnishes*, this occurring more readily if the oils are boiled with oxide of lead or of manganese.

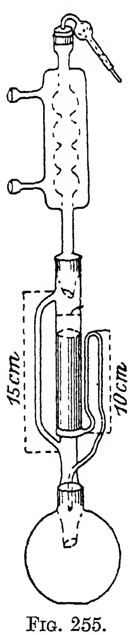

FIG. 255.

[1] To determine the quantity of fat contained in any solid substance, a weighed portion of the latter in a finely divided, dry state (5 to 15 grms. is taken and, if pasty, mixed with fragments of pumice) is introduced into a filter-paper cartridge situate in a *Soxhlet apparatus* (Fig. 255).

The Soxhlet apparatus is connected at the bottom with a tared flask resting on a water-bath, and at the top with a reflux condenser. From 100 to 150 c.c. of petroleum ether or ether is then added and extraction continued for 2 to 4 hours in such a way that the solvent siphons over 15 or 20 times per hour. A calcium chloride tube may be attached to the extremity of the condenser to prevent access of moisture from the air. The solvent is afterwards evaporated from the flask and the residual fat dried at 100° to 102° until almost constant in weight.

The difference between the weight of fat and that of the original substance gives the solids *not fat*.

With the other non-drying oils, the air (together with light) gradually causes *rancidity*, which, however, some attribute to the action of bacteria, or rather to hydrolysing and oxidising enzymes; however this may be, the acidity increases owing to formation of butyric, caproic, oleic, etc., acids, but the rancid taste and smell are due more especially to the formation of aldehydic, ketonic, and ethereal substances, hydroxy-acids, and volatile acids which can be eliminated by repeated washing with dilute solution of alkali and subsequently of bisulphite (for the aldehydes and ketones, *see later*, Renovated Butter).

When fats turn rancid, the *iodine number* [1] is lowered and the *index of refraction*,[2] the *dropping* or *melting point* (*see* pp. 5 and 6), and the *acetyl*

[1] The **Iodine Number** is characteristic of a fat (*see* Table, p. 466), and expresses the percentage of iodine absorbed by the fat (*i.e.*, by its unsaturated components, *e.g.*, oleic acid or the corresponding glycerides, two atoms of iodine being fixed for each double linking, *see* p. 107). This determination requires: (1) An *iodine solution* obtained by mixing, 48 hours before using, equal volumes of the two following solutions: (*a*) 25 grms. of iodine in 500 c.c. of pure 95 per cent. alcohol, and (*b*) 30 grms. of mercuric chloride in 500 c.c. of pure 95 per cent. alcohol; (2) a *sodium thiosulphate solution*, prepared by dissolving 24 grms. of the pure salt in a litre of water, the titre in iodine being ascertained as follows: 3·8657 grms. of pure, dry potassium dichromate is dissolved in water at 15° and the solution made up to a litre; exactly 20 c.c. of this solution is introduced into a flask with a ground stopper, about 15 c.c. of a 10 per cent. potassium iodide solution (free from hydroxide) being added and then 5 c.c. of concentrated hydrochloric acid. This procedure results in the liberation of exactly 0·2 grm. of iodine. The thiosulphate solution is then run in from a burette until the solution is only faintly yellow. A few drops of fresh starch-paste are then added and addition of the thiosulphate continued until the blue colour disappears. It is thus found how much iodine corresponds with 1 c.c. of thiosulphate solution, the strength of which remains constant for several months.

The iodine number is determined by dissolving a known weight of the fat or oil (0·2 to 0·5 grm. or, for drying-oils, 0·1 to 0·12 grm.), in a 500 to 800 c.c. flask with a ground stopper, in 15 c.c. of pure chloroform and adding 25 c.c. of the iodine solution (prepared 48 hours previously, as stated above); if, after two hours, the liquid is no longer very brown, a further measured volume of iodine solution is added and the whole left in the dark. After six hours the excess of iodine left unabsorbed by the fat is determined by adding 20 c.c. of 10 per cent. KI solution, diluting with 150 c.c. of water, and adding more KI if the reddish brown solution is not clear. The excess of iodine is then titrated with the thiosulphate solution in the manner already described. Immediately afterwards, 25 c.c. of the iodine solution employed is titrated. The difference between the two values thus obtained, expressed as grams of iodine per 100 grms. of the fat, represents the iodine number.

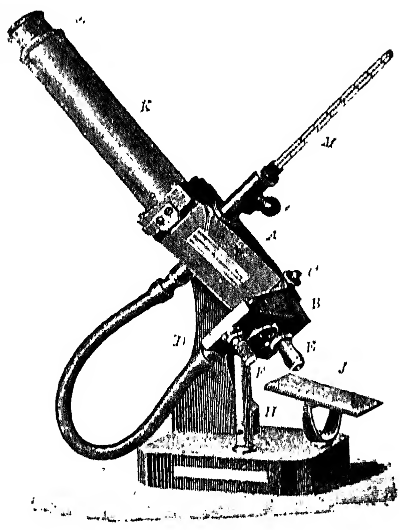

Fig. 256.

[2] The index of refraction is measured in the Zeiss **Butyro-refractometer** (Fig. 256), by observing the total reflection of a very thin layer of oil or fat situate between two prisms, *p*, mounted in the two chambers, *A* and *B* (the latter rotates on the hinge, *C*, so as to squeeze uniformly the film of oil smeared in *p*: the screw, *F*, fixes *B* against *A*). Indirect light from the sun or from a powerful sodium lamp is passed through the prisms by means of the mirror, *J*, and the limit between the light and dark portions of a scale reading from 0 to 100 is read through the eye-piece, *K*. A thermometer, *M*, indicates the temperature at which the observation is made, and this temperature may be regulated (so as to melt solid fats) by passing water, at a higher or lower temperature, in at *E* and through the rubber tube, *D*, to the outflow, *c*. The refraction is usually stated in the centesimal degrees of the Zeiss scale, the temperature -normally 25°- being indicated. Values obtained at other temperatures may be referred to the normal temperature by adding or subtracting 0·55 for each degree above or below 25° (the number 0·55 is accurate for butter, but slightly inexact for other fats).

The *index of refraction* is obtained from the reading on the Zeiss scale by adding to the value 1·4220 as many ten-thousandths as are obtained by multiplying the scale degrees by 7·8 when the reading is between 0 and 30; 7·5 if between 30 and 50; 7·3 if between 50 and 70; and 7·0 if between 70 and 100. (This procedure, too, gives accurate values for butter, but slightly inaccurate ones for other fats). Thus, 30° on the Zeiss scale would correspond with a refractive index of $1{\cdot}4220 + 30 \times \frac{7{\cdot}8}{10000} = 1{\cdot}4220 + 0{\cdot}0234 = 1{\cdot}4454$, which agrees almost exactly with

number (*see* p. 224) rise. In *butter* rancidity is facilitated by the presence of the casein and milk-sugar, which give rise to other decompositions. Although not rigorously exact, the *degree of rancidity* is expressed by the number of c.c. of normal potash necessary to neutralise 100 grms. of the fat. A *butter* with 10° of rancidity should be rejected. The free fatty acids in fats and oils are usually determined with a decinormal alkali solution, 5 to 10 grms. of the fat being dissolved in 50 to 60 c.c. of a perfectly neutral mixture of alcohol and ether (1 : 2) and phenolphthalein being used as indicator. The *acid number* gives the number of n grms. of KOH necessary to neutralise 1 grm. of fat.

By passing a current of air through oils heated to 70° to 120°, the so-called *blown* or *oxidised oils*, rich in triglycerides of hydroxy-acids, are obtained. These are dark in colour and have the density of castor oil (but are soluble in petroleum ether), but if "blown" in the cold for a longer time, they are obtained almost colourless. Blown oils are valued as lubricants. If the blowing is continued, yellow or brown gelatinous masses are obtained. With the exception of the iodine number and the Hehner number—which are lowered—the chemical and physical constants of blown oils (*thickened oils*, etc.) are higher than those of the original oils. Oils also fix *ozone* in proportion to the unsaturated fatty acids they contain, and at the same time become denser (*see* p. 359); olive oil has the *ozone number* 15·8 (grms. of ozone fixed per 100 grms. of oil: Fenaroli, 1906); maize oil, 21; linseed oil, 33; and castor oil, 16. Also *sulphur* is dissolved and combined in amount increasing with the proportion of glycerides of unsaturated acids present, giving very viscous, brown liquids, sometimes almost solid and gummy.

Chlorine acts on fats, partly replacing hydrogen and partly combining directly.

Iodine is added slowly, but the addition becomes rapid in alcoholic solution and in presence of mercuric chloride (Hübl).

Addition of concentrated **sulphuric acid** to oils results in the development of heat and the evolution of sulphur dioxide; in the cold, sulphuric ethers of the triglycerides are formed.[1]

Dilute **nitric acid**, in the hot, slowly oxidises fats, while the concentrated acid attacks them with evolution of red vapours.

Nitrous Acid renders non-drying oils denser and solidifies them, the triolein being converted into trielaidin (*see* p. 359); the drying oils remain liquid, although their specific gravity, viscosity, and saponification number increase, and the iodine number and Hehner number (per cent. of insoluble fatty acids) diminish.

When burnt, fats give the characteristic odour of acroleïn, which is derived from the glycerol.

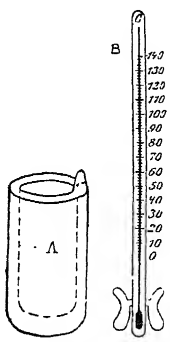

FIG. 257.

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the true index of refraction (1·4452); similarly, 60° on the scale means a refractive index of $1{\cdot}4220 + 60 \times \frac{7{\cdot}3}{10000} = 1{\cdot}4658$. Inversely, the scale reading is obtained by subtracting 1·4220 from the refractive index and dividing the remainder by 7·8, 7·5, 7·3, or 7·0.

The colour of the line of demarcation on the scale sometimes gives an indication of impurity in the fat, being colourless for pure butter, blue if margarine is present, and orange with admixtures of certain other fats.

[1] Maumené found that the rise of temperature produced by sulphuric acid of definite concentration serves to distinguish different fats (*see* Table given later). This constant (*Maumené number*) is nowadays determined by means of the *Tortelli thermo-oleometer* (1905). 20 c.c. of the oil is poured into the glass receiver, *A* (Fig. 257), the jacket of which has been evacuated. The oil is stirred for one minute with the thermometer, *B*, fitted with platinum vanes, and the initial temperature read. 5 c.c. of concentrated sulphuric acid (sp. gr. 1·8413 or 66° Bé.) is then added from a pipette in 30 seconds, the liquid being kept stirred as long as the temperature rises. The rise of temperature is the *Maumené number*. If the sulphuric acid has not the density given above, but is allowed to absorb even traces of moisture, discordant results are obtained.

On paper, fats and oils produce a translucent spot, insoluble in water (different from glycerol).

All these reactions serve as qualitative and quantitative tests to establish the purity of fatty substances (*see later*).

WAXES. Unlike fats, waxes are usually composed, not of triglycerides, but of esters derived from the higher monohydric alcohols (*e.g.*, cetyl, myricyl, and ceryl alcohols, cholesterol, etc.), and sometimes dihydric alcohols also. They contain, in addition, the high acids (*e.g.*, palmitic, stearic, cerotic, oleic, etc.) and alcohols in the free state. Further, beeswax contains as much as 15 per cent. of high melting-point hydrocarbons.

They form homogeneous mixtures in all proportions when fused with fats and give also a greasy spot on paper, but they yield no odour of acroleïn when burned (unlike fats) and do not become rancid when exposed to the air.

The commonest waxes are beeswax, Japanese wax, spermaceti wax (from whales), and carnauba wax (from the leaves of certain palms).

Beeswax forms the hexagonal cells of beehives. After the honey has been expressed, the mass is melted with water to remove impurities ; on cooling, a solid layer of crude wax separates at the surface, and this, after being melted and cast into blocks, forms *virgin* or *yellow wax*. This is placed on the market in various qualities and colours, some of them being olive-brown ; they bear the name of the place of origin and can be bleached with varying facility.

The European waxes have the following physical and chemical constants, which allow of the detection of the frequent adulteration to which they are subjected : melting-point, 62° to 64° ; solidification point, 60° ; specific gravity at 98° to 100°, 0·822–0·847 ; saponification number, 95 to 97 (rarely 88 to 105) ; acid number, 19 to 22 ; difference between saponification number and acid number (*ester number*), 74 to 76 ; iodine number, 8 to 11 ; degrees on the Zeiss butyro-refractometer at 40°, 44 to 45·5 (rarely 42). Foreign waxes have somewhat different constants.

The bleaching of the wax is effected by melting it several times with slightly acidified water, allowing it to cool slowly so as to separate the impurities more thoroughly and then causing it to solidify in thin layers on a cylinder half immersed in water and exposing these to the sun and air for five to six weeks. A more expeditious method of bleaching consists in treatment with hydrogen peroxide or other oxidising agent (dichromate and dilute sulphuric acid), or with animal charcoal. The *white wax* thus obtained—often improved in appearance by the addition of 4 to 5 per cent. of tallow—presents almost the same physical and chemical constants as the virgin wax, the iodine number alone being lowered by 1 to 7.

The wax is insoluble or only slightly soluble in cold alcohol or ether, but dissolves in the boiling solvents. It dissolves in the cold in chloroform, oil of turpentine, carbon disulphide, or fatty oils. It resists dilute caustic alkalis and concentrated alkali carbonates. It is used for making candles, waxed cloth and paper, mastics, artificial fruit and flowers, etc.

Carnauba wax is exuded from the leaves of certain palms (*Corypha cerifera*) of Brazil and Venezuela. In the crude state, it is hard and brittle, and of a yellowish green colour ; it melts at 83° to 88°, has the acid number 4 to 8, the saponification number 80 to 95, the ester number 75 to 76, and the iodine number 7 to 13, and contains more than 50 per cent. of non-hydrolysable substances. It is used for the manufacture of candles and, mixed with potash (soft) soap, forms the *encaustic* with which pavements are cleaned.

Japanese wax is the fat extracted from the fruit of certain Japanese and Chinese trees of the order Terebinthaceæ (*Rhus succedanea, R. vernicifera,* and *R. sylvestris*). It differs from beeswax in having an ester number of about 200 and a saponification number of about 220. It is completely hydrolysable, since it consists of glycerides of palmitic, stearic, and arachic acids, and contains also 9 to 13 per cent. of free palmitic acid.

Uses. Wax was formerly used mostly for making the wax candles prescribed for religious ceremonies in Roman Catholic churches, and about the beginning of the present century the Holy Synod of the Orthodox Russian Church rendered obligatory the use of candles of beeswax. Admixture with beeswax of stearin, paraffin wax, and various other substances is, however, not easy to detect by analysis.

Before the European War, yellow beeswax cost up to £150 per ton and the bleached wax £170.

PHYSICAL AND CHEMICAL CONSTANTS OF OILS, FATS, AND THE CORRESPONDING FATTY ACIDS

	Specific gravity at 15°	Solidifying point		Melting-point		Hehner number	Acetyl number	Reichert-Meissl-Wollny number	Saponification number mgrms. KOH		Iodine number		Maumené number	Butyro-refractometer reading	Index of refraction at 60°
		Fat	Fatty acids	Fat	Fatty acids				Fat	Fatty acids	Fat	Fatty acids	Fat	Fat	Fatty acids
Vegetable Oils and Fats															
Linseed oil	0·9315–0·9375	−16° to −27°	13°–17°	−20°	17°–21°	95·5	4–8	—	192–195	197	171–195	179–198	110–126	72·5 at 40°	1·4546
Hempseed oil	0·9255–0·9280	−27°	15°	—	18°–19°	—	—	—	172–192	—	148	141	97	—	—
Poppyseed oil	0·9240–0·9370	−18°	15°–16°	—	20·5°	95·2	—	—	195	199	133–143	139	86–89	63·4 at 40°	1·4506
Maize oil	0·9213–0·9255	−20°	16°–14°	—	18°–20°	—	8	—	188–193	198·4	116	119–125	95	67	—
Cottonseed oil	0·9220–0·9310	—	32°–35°	3°–4°	36°–38°	95–96	8–18	—	193–196	202–208	108–110	111–115	75–90	68·5 at 25°	1·4460
Sesamé oil	0·9230–0·9237	−5°	21°–23·5°	—	26°–32°	95·7	11·5	1·2	189–193	200·4	103–108	110·4	65	68 at 25°	1·4461
Colza oil	0·9132–0·9168	−2° to −10°	16°	—	16°–22°	95·1	14·7	0·3	170–179	185	94–102	99–103	55–64	68 at 25°	1·4991
Castor oil	0·9600–0·9679	−10° to −18°	3°	—	13°	94	147–150	1·4–2·8	183–186	192	83–86	87–93	46·5	78 at 25°	1·4546
Almond oil	0·9175–0·9195	−10° to −20°	5°–10·5°	—	13°–14°	96·2	—	—	191	204	93–102	93–96·5	52·5	64·4 at 25°	1·4461
Arachis oil	0·9170–0·9209	−3° to −7°	26°–29°	—	27·7°–32°	95·8	—	—	190–196	201·6	83–100	96–103	45–51	67 at 25°	1·4461
Olive oil	0·9160–0·9180	−6° to +2°	22°–17°	—	24°–27°	95	10·6	0·3	185–196	193	79–88	86–90	41–45	62·4 at 25°	1·4410
Palm oil	0·9210–0·9245	—	36°–45°	27°–42°	47°–50°	95	18	0·5	196–202	205·6	51·5	53·3	—	—	1·4510
Palm-kernel oil	0·9520	20·5°	20°–25°	23°–28°	25°–28°	87·6–91	2–8	5–6	242–250	258–264	13–14	12	—	36·5 at 40°	1·4310
Grapeseed oil	0·9258–0·9262	—	—	—	—	92·6–93·7	23–25	0·35–0·40	190–195	—	130–140	—	—	—	—
Cacao-butter	0·9500–0·9760	23°–21°	47°–45°	28°–33°	48°–50°	94·6	2–8	1–4	193·5	190	32–41	33–39	—	47 at 40°	1·4220
Coconut oil (butter)	0·9115–0·9250	22°–14°	20°–16°	21°–24°	25°–27°	84–90	1–12	7–8·4	246–260	258–266	8–9·5	8·4–9·3	—	34 at 40°	1·4295
Soja-bean oil	0·9255	−8° to −16°	22°	—	27°	95·9	—	0·45	192·9–193·5	—	125	—	86–87	—	1·4750 (at 20°)
Animal Fats															
Ox fat (tallow)	0·9430–0·9520	35°–27°	38°–46°	45°–40°	43°–44°	95·6	3–8	0·25	193–200	197	38–46	41·5	—	49 at 40°	1·4375
Bone fat	0·9140–0·9160	15°–22°	28°	21°–22°	30°	86–94	11	—	191	200	46–56	55·7	—	—	—
Horse fat	0·9189	43°–30°	37·7°	37°–43°	37·5°–39·5°	95·5	—	0·3	196	202·6	71–86	84–87	—	53·7 at 40°	—
Butter	0·9260–0·9400	20°–23°	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	—	[illegible]	[illegible]
Hog's fat	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

Hydrolysis (Saponification) of fats and waxes.—The term saponification is applied to the decomposition of fats into the alcohols and acids composing them with simultaneous addition of a molecule of water (*hydrolysis*), by heating with water under pressure at 200° or by the action of acid or alkali (*see* p. 458); when alkali is used, the alkali salt (soap) of the fatty acid and not the free acid itself is obtained:

$$\underset{\text{Tristearin}}{C_3H_5(O \cdot OC_{18}H_{35})_3} + 3KOH = \underset{\text{Glycerine}}{C_3H_5(OH)_3} + \underset{\text{Potassium stearate}}{3C_{18}H_{35}O_2K.}$$

The mechanism of the saponification of fats was for long a matter of controversy. Some regarded it as occurring gradually, 1 mol. of fat first reacting with 1 of alkali (bimolecular reaction) (*see* Vol. I., p. 69) and di- and monoglycerides being formed as intermediate products, whilst, according to others, saponification was a single (tetramolecular) reaction. Only since the investigations of Geitel (1897), Lewkowitsch (1898–1901) and, more especially, Kremann (1906), does it appear to be established with certainty that saponification is gradual, consisting of successive bimolecular reactions. Contrary to the view of Fortini (1912), J. Meyer (1913) showed that the various glycerides, glycerol, and soap occur together in an equilibrated mixture, the equilibrium undergoing gradual displacement towards complete saponification, as was indicated by the results of Kellner (1909) and of Kremann (1905–1908).

Saponification with lime, baryta, or lead oxide is never so complete as with caustic potash or soda in the hot, while with an alcoholic solution of caustic potash or soda it is complete and rapid, formation of the ethyl ester of the fatty acids and liberation of glycerine first occurring and then complete hydrolysis of the ethyl ester. The latter may be obtained directly from fats by heating them with slightly acidified alcohol.

Sodium and potassium carbonates do not attack fats.

Fats may be saponified by treatment with a small proportion of aqueous ammonia in an autoclave, but the early attempts to render this process practicable on an industrial scale were unsuccessful. The reaction was, however, investigated systematically by Garelli, Barbé and De Paoli, who obtain complete saponification by heating the fat for seven to eight hours in a lead-lined autoclave under a pressure of 6 atmos. with a minimum amount of ammonia (0·6 per cent.), which acts catalytically and liberates the fatty acids. This process is undoubtedly an improvement on the lime, magnesia and zinc oxide processes, but since the ammonia cannot be recovered, it cannot compete with the enzymic decomposition of fats in open wooden vats at comparatively low temperatures (*see later*). The use of 6 to 7 per cent. of ammonia, as proposed by Buisine (1883), or even of 2 to 3 per cent., in an autoclave leads to serious difficulty owing to the formation of a completely emulsified mass of ammonia soaps which do not allow the glycerine solution to separate, and to the trouble and expense of treating the ammonia soaps with steam to separate the fatty acids. Garelli, Barbé and De Paoli (Ger. Pat. 209,537, 1906) transform the ammonia soaps directly into soda soaps by simple treatment with sodium chloride, just as in the Solvay soda process (Vol. I., p. 596); the recovery of the ammonia is, however, difficult and the loss exceeds 8 per cent.

A process patented some years ago for saponifying fats by means of sulphur dioxide or bisulphite in autoclaves at 10 to 15 atmos. offers no promise of practical application.

No matter how difficult the saponification of a fat, it may be rendered complete even in the cold by the Henriques process, which consists in dissolving, say, 3 to 4 grms. of the fat in 25 c.c. of petroleum ether and 25 c.c. of normal alcoholic potash, the mixture being shaken from time to time during a period of twelve hours; on heating, waxes are also dissolved in this manner.

To determine the quantity of alkali fixed (*saponification number*),[1] the excess of alkali is titrated with normal acid solution.

Dilution of the saponified waxes with a considerable amount of water results in the separation of the higher alcohols, which can be extracted with ether. Spermaceti contains 40 to 60 per cent. of these insoluble alcohols (which are known industrially as non-saponifiable substances), beeswax 53 per cent., and carnauba wax 55 per cent.

ANIMAL OILS AND FATS

It is not possible here to study in detail all fats, so that only the more important ones, the processes of treating which are partially applicable to the others, will be considered.

Classification of fats into those of animal and those of vegetable origin or into solids (tallow, lard, sheep's tallow, goose grease, and coconut butter) and liquids (oils) is of no practical value, but it is necessary, with the liquid vegetable fats, to distinguish between those which have *drying* (linseed, walnut, poppyseed) and those with *non-drying* properties (olive, colza, arachis, castor, cottonseed, maize, etc.).

Animal fats are usually melted (by direct-fire heat or by steam) or compressed either hot or cold, although sometimes they are extracted with solvents. Vegetable oils are extracted from the disintegrated seeds by pressing them hot or by treatment with suitable solvents. In both cases they are refined by a series of mechanical and chemical operations which will be described more particularly in dealing with tallow, butter, and olive oil.

TALLOW (ox fat, sheep fat, etc., but not hog's fat) melts at 35° to 37°, contains 75 per cent. of stearin and palmitin (in equal parts) and 25 per cent. of olein. In the crude state, as it comes from the slaughterhouse, it is incorporated in a cellular tissue and contains various impurities, such as blood, skin, etc., which gradually putrefy, giving a bad odour to the tallow. To prepare the real fat from the crude tallow, the latter is cut up in suitable machines fitted with knives and is then melted in open iron or copper boilers provided with stirrers and heated either wholly by direct-fire heat or partly in this way (Fig. 258) and partly by injecting direct steam, superheated to 180° to 200° through the tube, *D*. The strongly smelling gases evolved are led by the pipe, *a*, under the hearth and there burned.

[1] The Saponification number, or *Köttstorf number*, indicates the number of milligrams of KOH necessary to saponify 1 grm. of fat or wax completely. The determination is made as follows: 1·5 to 2·2 grm. of the filtered fat is weighed into a 150 to 200 c.c. wide-necked flask, to which is then added 25 c.c. of seminormal alcoholic KOH solution prepared with 90 per cent. alcohol and also 25 c.c. of neutralised alcohol. The mixture is then heated for 15 to 20 minutes in a reflux apparatus on a water-bath previously heated to boiling, and, while still tepid, is titrated with seminormal hydrochloric acid (not sulphuric acid, which would precipitate K_2SO_4), using phenolphthalein as indicator. Multiplication of the number of c.c. of seminormal KOH solution actually consumed in the saponification by 0·0301 gives the number of mgrms. of KOH, which is calculated for 1 grm. of the fat.

Non-saponifiable substances (mineral oils, etc.) added to fats as adulterants can be detected by the following qualitative test devised by Holde: two drops of the oil are boiled for one minute with a solution of a piece of caustic potash the size of a pea in 5 c.c. of boiling absolute alcohol, 3 to 4 c.c. of water being afterwards added to the liquid; in presence of as little as 1 per cent. of non-saponifiable compounds, a turbidity is produced. Also a benzene solution of picric acid gives a red coloration with fat containing 1 per cent. of mineral oil.

For detecting traces of *neutral fats* (non-saponified) in pure *fatty acids* of commerce, *Geitel's test* is employed: 15 c.c. of ammonia solution is added to a solution of 2 grms. of the fatty acids in 15 c.c. of hot alcohol. Turbidity of the liquid indicates the presence of much neutral fat. If, however, the liquid remains clear, cold methyl alcohol is poured carefully on to its surface; a turbid ring is formed between the two layers of liquid in presence even of traces of neutral fats (this test does not answer with palm oil).

The *addition of resin* to fat is discovered by the Liebermann-Storch-Morawski test applied to the fatty acids obtained in determining the Hehner number (*see* p. 461): a few drops of cold sulphuric acid of 50° Bé. are added to a well-cooled solution of 1 to 2 grms. of the fatty acids (which contain the resins) in 1 c.c. of acetic acid. If traces of resin (pine or colophony) are present, an intense red or violet coloration forms immediately and rapidly gives way to a brown fluorescence (presence of cholesterol or wool-fat produces a reddish brown coloration, which changes to blue and then to green).

The clear, molten fat, after a long rest, is discharged through the tap, *E*, and filtered through a bag, the solid fragments of cellular membranes and other impurities being retained by a perforated double bottom. These impurities, while still hot, are squeezed in a press such as that made by C. E. Rost, of Dresden (Fig. 259), being placed inside the perforated cylinder, *a*, which is surrounded by the jacket, *h*, and closed by the cover, *b*,

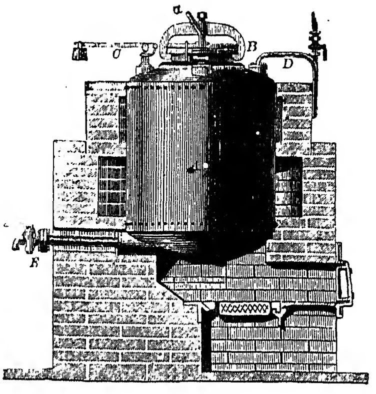

FIG. 258.

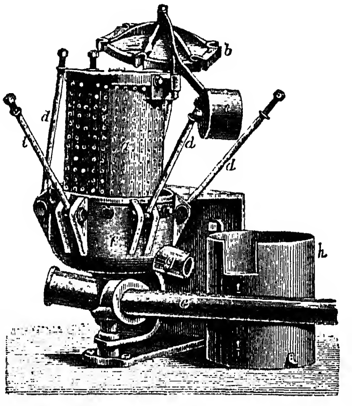

FIG. 259.

fixed by the screws, *d*; the pressure is exerted underneath on a plate raised by means of the lever, *e*. The pressed residue is then either treated with carbon disulphide to recover the small amount of fat still retained, or used directly as cattle-food. A powerful press, which is largely used, is shown in Fig. 260.

Fusion of Tallow with Acid (d'Arcet method). This method increases the yield and improves the flavour of the tallow. It is carried out in the Fouché apparatus (Fig. 261), consisting of a closed boiler, which can be heated both by indirect steam circulating through

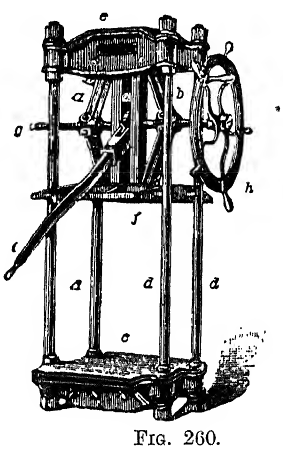

FIG. 260.

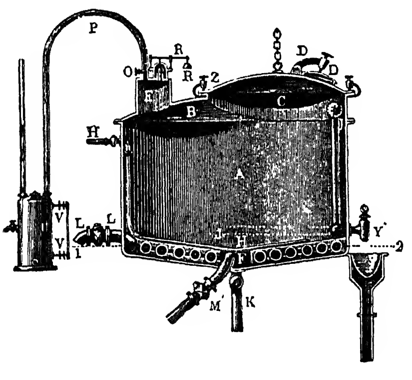

FIG. 261.

a coil on the bottom and by direct steam issuing from a perforated pipe passing also to the bottom. 100 kilos of tallow are mixed with 50 kilos of water containing 1 kilo of sulphuric acid of 66° Bé., the whole being heated for two hours at 105° to 110°. The clear, fused fat floats on the surface of the acid solution, which is replaced by pure water, the tallow being heated and mixed with the latter by means of direct steam; after some time, the washed tallow is discharged from a lateral tube—which, inside the vessel, is free and floats—through a cloth bag. When this acid process is used, the solid fragments separated cannot be used for feeding cattle.

Fusion with Alkali. Evrard heats the tallow with a very dilute solution of sodium

carbonate, while Rorard treats 1000 kilos of the tallow with 200 of water containing a kilo of caustic soda, the mixture being then melted at 100° in the Fouché apparatus. The alkaline process gives a diminished yield and does not diminish the amount of pungent gases evolved.

Refining. If the fusion, especially when acid is used, has been successfully carried out, refining is usually unnecessary. It is, however, required when the tallow is to be used for food or for fine soaps; that employed for candles is sometimes bleached. In general, it is heated and stirred with water for a long time in suitable vats. It is then left at rest until it separates from the water and is filtered through a cloth bag and collected in a tank, heated outside in order to retard solidification and give time for any further impurities present to deposit.

If the fused tallow is allowed to cool slowly at a temperature above 28°, it sets to a granular mass, as crystals of stearin and palmitin first separate; from this mass the olein is more easily removed by subsequent compression.

Many different processes have been suggested for the *bleaching* of tallow, but the only ones deserving of mention here are those consisting in heating with animal charcoal, bone-black, and fuller's earth (magnesium hydrosilicate, *see* pp. 80, 89, and Vol. I., p. 738), and then filtering, and those in which, say, 1000 kilos of tallow is heated with a solution containing 20 kilos of water, 10 of concentrated sulphuric acid, and 5 of potassium dichromate (or 60 kilos of concentrated hydrochloric acid and 15 of permanganate at 40°); after stirring, the mixture is left for a time and then washed several times with hot water. In some cases, the tallow is stirred and heated to 40° with 25 kilos of an aqueous solution containing 250 grms. of potassium permanganate, and 250 gms. of concentrated sulphuric acid, and well washed with hot water, a little sodium bisulphite being finally added. Chlorine, which is sometimes used for vegetable oils, is harmful to animal fats. Excellent results have been obtained recently by bleaching with sodium hydrosulphite (Vol. I., p. 586). Certain fats can be well bleached at 80° to 100° with 1 to 2 per cent. of barium peroxide, which is added gradually and with continual stirring. Fats and fatty acids are sometimes *deodorised* by treating with 20 per cent. of concentrated sulphuric acid at 30° to 40°, and then distilling the fatty acids under reduced pressure.

The purity of tallow is determined by the analytical methods already given (*see also* Table on p. 466), and for industrial purposes the *solidification temperature* of the fatty acids obtained by the Hehner method (*see* p. 461) is measured by introducing them in the fused state into a double-walled test-tube (best, that of the Tortelli thermo-oleometer, p. 464) and stirring with a thermometer until they begin to turn turbid. The temperature then ceases to fall and at a certain moment rises (the heat of solidification being developed) and remains constant until the whole mass has solidified; this constant temperature is that of solidification and, for good tallow, should be at least 43°. Adulteration with *cottonseed oil* is detected by *Halphen's reaction:* a mixture of 20 c.c. of the fat, 20 c.c. of amyl alcohol, and 2 c.c. of a 1 per cent. solution of sulphur in carbon disulphide is boiled in a test-tube; after about ten minutes' heating, a dark orange or red coloration will appear if even as little as 5 per cent. of cottonseed oil be present. If no coloration is evident after the lapse of ten minutes, a little more carbon disulphide may be added and the heating continued ten minutes longer. If the suspected tallow or the cottonseed oil before addition to the tallow were heated to 200° to 250°, Halphen's reaction would not be given.

The greater part of the tallow made is used in the manufacture of soap and candles, but an appreciable proportion is employed in margarine factories (*see below*). A well-fattened ox may give as much as 100 kilos of crude tallow.

Continental Europe imports large quantities of tallow from America, Australia, and England. The price varies somewhat, and, while in 1870 it was £40—£56 per ton, in 1884 it was £33, in 1885 £28, in 1886 £22, in 1888 £27, in 1892 £24, and in 1893 £27; in 1906 the price on the Italian markets varied from £28 to £31, in 1907 from £32 to £36, and in 1908 from £30 to £33.

France imported 16,500 tons of tallow in 1913, 17,190 tons in 1914, and 10,180 in 1915.

Germany imported 6226 tons of tallow in 1888 and almost 11,000 tons in 1891 (*see later*, Importation of melted tallow for oleomargarine).

In 1909 England imported 110,000 tons of tallow and stearin, and in 1910 123,150 tons, while the United States exported 8500 tons in 1910 and 22,000 tons in 1911.

OLEOMARGARINE and **MARGARINE** (Artificial Butter). The oleomargarine obtained

from tallow serves to prepare margarine or artificial butter by churning it up with milk. It is also used to some extent for making the so-called *margarine-cheese* from separated milk. the butter being replaced by oleomargarine, which is incorporated by means of emulsifiers.

It was Napoleon III. who, on account of the rise in price of provisions and more especially of butter, offered in 1870 a prize for the discovery of a cheap fat to replace butter, and placed at the disposal of the inventor a large works at Poissy, near Paris, adapted to the development of the industry. The prize was awarded in 1871 to the Mège Mouriès process for the manufacture of oleomargarine from tallow by a method which is almost identical with that used at the present day (the addition of sheep's stomach to render soluble the cellular membranes enveloping the fat has now, however, been abandoned). As early as 1873 30 tons of margarine was consumed in Paris.

As a rule, oleomargarine factories are situated close to the slaughterhouses, so that the tallow may be obtained fresh from the animals. The tallow is cooled immediately by washing it in a current of cold water, which removes the blood and other impurities, and if it cannot be worked at once is hung in separate pieces in a cold chamber.

The tallow is then cut up and introduced, with one-fourth of its weight of water at 55°, into a vat similar to that used for the melting of tallow (*see* p. 468), but nowadays the heating and melting are effected by the circulation of hot water at 60° to 70° instead of steam, so as to avoid scalding the mass. The latter is kept slowly stirred and a couple of hours is sufficient time to melt 2000 kilos of tallow, which floats on the water, whilst the bits and membranes are deposited on the bottom ; this separation is facilitated by the addition of 2 per cent. of salt, previously dissolved in water.

After the mass has remained at rest for some time, all the impurities settle and the molten fat is removed by a tap connecting inside the vat with a free, floating tube which gradually falls as the layer of fat diminishes : the latter is collected in tinned, double-walled tanks surrounded by hot water, so that further clarification may result on long standing. The fat then bears the name *premier-jus* and is mixed in small proportion into margarine, while the remainder is poured into flat, tinned moulds holding about 20 kilos and allowed to solidify in a chamber kept at a temperature of about 30°.

The semi-solid mass thus formed is placed in cloths and squeezed—not too strongly—in hydraulic presses (similar to those used in making stearic acid for candles, *see later*) in a room at about 25°. This procedure yields about 45 per cent. of a solid residue of stearin (for candles) mixed with a little olein, and a liquid product (55 to 60 per cent.) composed of 55 per cent. of triolein, 35 per cent. of tripalmitin, and 10 to 15 per cent. of tristearin ; this is *oleomargarine*, which assumes an almost pasty consistency at ordinary temperatures and has a yellow colour and a pleasant odour similar to that of butter.

It is used in some cases as fat for cooking, but usually it is converted into artificial butter.

Oleomargarine has the sp. gr. 0·859 to 0·860 at 100°, melts at 33·7°, has the Hehner number (*see* p. 461) 95·5, the Reichert-Meissl-Wollny number (*see* p. 461) 0·4 to 0·9, and the iodine number (*see* p. 463) 44 to 55.

MARGARINE (or **Artificial Butter**) is prepared from oleomargarine, from one-tenth to one-fifth of sesamé or arachis or even cottonseed oil being added for the lower qualities (in America maize oil is used). In some countries no milk is now used, attempts being made to flavour the oleomargarine directly with certain strongly flavoured cheeses prepared for this express purpose, or with butyric acid or its homologues, or with a special flavouring placed on the market under the name of *margol.*

It is necessary that artificial butter, when fried, should give the same smell as natural butter, and this result is attained partly by adding a little cholesterol (Ger. Pat. 127,376) to the milk used to render the oleomargarine pasty. Margarine is also required to brown and froth like natural butter when fried, and this is attained by adding about 2 per cent. of egg-yolk (Ger. Pat. 97,057) or 0·2 per cent. of lecithin (a constituent of yolk of egg ; Ger. Pat. 142,397) and a small quantity of glucose, while it has also been proposed to add a little powdered casein, egg-yolk and pasteurised milk-cream (Ger. Pat. 170,163).

The yellow colour of commercial, natural butter is imitated by the addition of a little *butyroflavine* (dimethylaminoazobenzene) dissolved in sesamé or cottonseed oil (placed on the market by the Société Fab. de Produits Chimiques de Thann et de Mulhouse).

In the manufacture of *first-quality margarine*. the fats to be mixed (*e.g.*, for summer margarine, 600 kilos of oleomargarine, 30 kilos of premier-jus (*see above*), and 60 kilos of

sesamé oil; for winter margarine, the premier-jus is replaced by a similar quantity of sesamé oil) are first melted separately at 40° to 45°. For inferior margarines, less oleo-margarine, more premier-jus, and a certain amount of cottonseed oil are used. Half of the molten, homogeneous fat is introduced into a churn (that of H. Grasso, of Hertogenbosch, Holland, Fig. 262, gives good results) containing 300 litres of milk [1] previously churned to the clotting point and mixed with 50 grms. of colouring solution; 0·1 per cent. of glycerine is sometimes added to render the mixing more complete. The churn has a closely-fitting lid and is jacketed so that it can be surrounded with water at 35° to 45°; it is fitted with stirrers (120 revs. per minute) and the inner surface is thickly tinned. After 10 to 15 minutes' churning the remaining half of the milk and molten fat is introduced, the churning being continued for a further period of 20 to 25 minutes. When the mass has reached a temperature of 30° to 45° (better quality but diminished yield is obtained at 30°), it is allowed to flow into a shallow double-walled vessel cooled by the circulation of water at 0° to 2°, and, as it flows, it is washed with a powerful jet of water at 2° and is constantly mixed with wooden blades. The wash-water is then run off and the hardened, disintegrated mass left overnight so that the wash-water may separate better. A *homogenising machine* of the Schroeder type has been introduced recently, and this allows of continuous working and effects a far more perfect mixing of the fats and milk, while it yields a more aromatic and stable product.

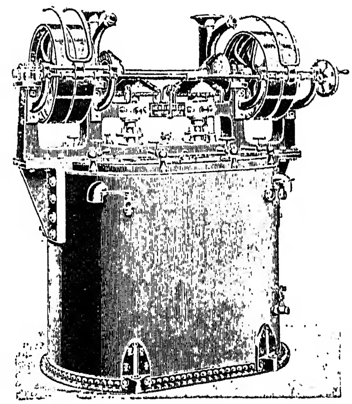

FIG. 262.

To complete the separation of the whey and washing-water, and to obtain a homogeneous pasty mass, the cold mixture is introduced gradually into an ordinary butter kneader (Fig. 263) with rotating base, this being situate in a cold chamber. After passing under the grooved cone eight or ten times, the mass is collected in blocks, which are left for 24 hours. If it is desired to mix a little cream or the allowed quantity of water (10 to 12 per cent.) into the mass, the latter is introduced into the Werner-Pfleiderer *kneader* (similar to that used for kneading bread), which can easily be reversed so as to expel the excess of liquid and finally the paste itself (Fig. 264).

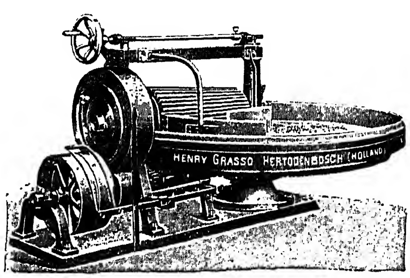

FIG. 263.

The margarine thus obtained is made up into cakes by means of suitable moulds bearing the trade mark and is then wrapped in parchment-paper previously disinfected in brine. In some countries this paper is marked with coloured stripes to allow the public readily to distinguish margarine from butter, and in all countries it is obligatory to exhibit margarine for sale in shops with a placard which distinguishes it from butter. In Germany and Austria the law requires margarine to be prepared with at least 10 per cent. of sesamé oil and not more than 10 per cent. of butter; by this means, the detection of butter adulterated with margarine is facilitated, as, owing to the sesamé oil present, it gives the *Baudouin reaction* for furfural.[2] If more than

[1] For the finer margarines, cream is used, but for ordinary varieties skim-milk from the separators is employed. In all cases, in order to obtain a margarine which will keep, even in summer, the milk is pasteurised at 55° to 60° and then subjected to slight acid fermentation with pure cultures of bacteria, which are sold by butter manufacturers.

The cooled milk is kept in clean, closed vessels in a cool place, and is consumed as soon as possible so as to avoid contamination. It may be centrifuged after pasteurising and cooling. If it is not rendered acid, the milk, and also the butter obtained therefrom, keep badly and do not incorporate well with the other fats.

[2] 10 c.c. of margarine, filtered into a separating funnel, is shaken for half a minute with 10 c.c. of HCl (sp. gr. 1·125). If the acid is coloured red, it is decanted off and the residue shaken with a fresh quantity of the acid. After removal of the acid, 5 c.c. of the fat is poured into a graduated cylinder with a ground stopper, where it is shaken with 10 c.c. of HCl (sp. gr. 1·19)

10 per cent. of butter is added to margarine the Reichert-Meissl-Wollny number (*see* p. 461) exceeds 2·5.

Normal margarine contains 8 to 9 per cent. of water and 1 to 2 per cent. of NaCl, and has the saponification number 193 to 203 (coconut fat raises this number to 220 and the Wollny number to 5) and the iodine number 52 to 60.

The experiments of Lührig (1900) have shown with certainty that margarine is digested by man as well as butter.

In 1911 many cases of fatal poisoning occurred in Germany owing to the use in margarine of cardamom oil (or Marotti fat) which may contain the poisonous chaulmoogric acid, $C_{18}H_{32}O_2$, m.-pt. 69°, and possibly also hydnocarpic acid, $C_{16}H_{28}O_2$, m.-pt. 60·4°, which is likewise poisonous.

The consumption of margarine, which costs little more than half as much as butter, is continually increasing in all countries. Germany possessed 55 factories in 1886 and 83, employing 1555 workmen, in 1895; and in 1899 produced 91,000 tons (worth more than £3,800,000) of first- and second-quality margarines, 55,000 tons of animal fats, 23,000 of vegetable fats and oils, 53,000 of skim-milk, and 4800 of salt being employed. Germany imported 28,500 tons of oleomargarine in 1906 and about 23,000 tons in 1909, and exported 297 tons of artificial butter in 1906 and 525 in 1909. In North Germany, margarine of first quality is used, but in the South margarine without butter and without milk.

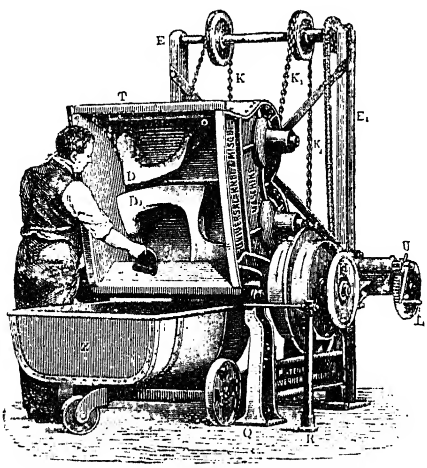

FIG. 264.

In 1907 there were 31 margarine factories in Norway. Thirty-seven factories existed in the United States in 1886, and the output, which was less than 6000 tons in 1902, rose to 45,000 tons in 1908 and 70,000 in 1910 (almost all not coloured), the exports being 1550 tons in 1910 (almost all coloured). In 1910–1911 the output in the United States fell to about 65,000 tons. In Denmark 22 factories produced 30,000 tons in 1909 and 34,300 tons in 1910, when the exports amounted to 1100 tons. England imported 1650 tons of oleomargarine in 1909 and 4050 tons in 1910 and exported 3295 tons in 1909 and 8138 tons (£206,360) in 1910. The principal exportation from the United States consists of the prime material, *oleo oil*, which is largely used in other countries for preparing the different margarines or artificial butters; in 1910, 50,000 tons of this oil (of the value of £2,360,000) and 1700 tons of oleomargarine (£80,000) were exported, and in 1911, 77,000 tons of oleo oil (of the value £3,120,000), and 18,000 tons of oleomargarine (£84,000). In 1907, Sweden produced 15,000,000 kilos, and in Holland there are over 100 factories. The total output of Holland and Belgium in 1910 was 65,000 tons (of the value £3,600,000), about 48,000 tons being exported. In Paris, more than 30 tons of margarine were manufactured per day as early as 1875. In Italy, the first factory, that of Regondi and Chierichetti, was erected in 1874 at Milan, with branches in Rome and Tuscany; even in 1888 this firm produced almost 400 tons of margarine, and at the present time, as a company (Chierichetti and Torriani), it still occupies the premier position. A considerable amount of suspicion was removed from the industry in Italy as the result of a valuable report prepared for the Royal Italian Society of Hygiene by Körner and Gabba in 1888, and in 1911 the consumption (largely for adding to butter) reached about 8000 tons; the importation of artificial butter was 121 tons in 1908, 64 tons in 1910, 49 tons in 1914, 119 tons in 1916, and about 500 tons in 1919 and 1920, while the amount exported (tons) was 216 in 1908, 286 in 1911, 803 in 1914, 47 in 1915, and 5 in 1919. In the Customs returns for Italy oleomargarine is included with other fats, so that the quantity imported is not known.

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and 0·1 c.c. of 1 per cent. solution of furfural in alcohol (absolute) for half a minute. If, after standing, the layer of acid shows an *intense* red coloration, the margarine contained the required quantity of sesamé oil. This reaction has, however, been criticised as being in some cases indecisive.

Owing to the high price of tallow in recent years, attempts have been made to prepare margarine by the addition of coconut oil in the kneader, after complete expulsion of the water (so as to prevent rancidity). There is now on the market margarine which bears the name of *cunerol* (or *kunerol*), and is made exclusively from coconut oil kneaded and treated with a saline solution of yolk of egg (instead of milk).

BUTTER is the fat obtained from *milk*,[1] in which it occurs emulsified in small drops

[1] MILK is a liquid secreted by female mammals after parturition, and serves as the first nutriment of the offspring, but that of certain animals (cows, goats, etc.) has been largely used, from the earliest times, for feeding infants and adults, and for the preparation of cheese, casein, milk-sugar, etc. The mean daily consumption of cows' milk per head is about 200 grms. in England, 450 in Canada, 600 in Holland, 260 in Paris, 600 in Munich, and 150 in London. The supply of milk to large towns constitutes a serious problem, since, for example, Genoa consumes 500 hectols. per day, Turin 700, Milan 1300, Berlin 8000, Paris 9000, and New York 16,000. In 1908 the United States exported £3,200,000 worth of *condensed milk* to China, Japan, the Philippines, Corea, Russia, Africa, and Mexico. The number of cows in France in 1909 was 7,336,000, and the yield of milk 132,000,000 hectols. Hungary in 1909 produced 26,000,000 hectols. of milk. In 1913 the large Swiss companies exported condensed milk to the value of £2,000,000. In 1903 Australia obtained from 1,300,000 cows about 16,000,000 hectols. of milk, 50,000 tons of butter (one-third being exported), and 6000 tons of cheese (barely one-fifth exported). In the United Kingdom 4,000,000 cows produced in 1909 about 72,000,000 hectols. of milk. In 1910 Norway produced 10,000,000 hectols. of milk. Germany possessed 10,000,000 cows in 1917.

In Denmark the dairy industry has attained a high degree of perfection, 1150 co-operative dairies treating 77 per cent. of the total milk produced in 1909. Marked improvements have been effected in the selection of milk cows and in their feeding, the mean yield of milk per cow increasing from 1400 kilos in 1884 to more than 2600 in 1912; the number of cows was 900,000 in 1881 and about 1,030,000 in 1912.

The *mean percentage composition* of the milk obtained by *complete* milking is found from some thousands of different analyses to be as follows: water, 87·22; fat, 3·62; nitrogenous substances (casein and a little albumin), 3·66; milk sugar, 4·82; and mineral matter, 0·68. The *casein* forms a kind of colloidal solution, which holds, in an emulsified and suspended condition, fat-drops of varying magnitude (diameter, 0·01 to 0·0016 mm.). Casein in milk occurs, indeed, in the form of a non-reversible hydrosol (*see* Vol. I., p. 106) and its coagulation by acids or heat can be retarded or prevented by the presence of a reversible colloid (*protecting colloid*, like gelatine or gum). In *cows' milk* the relation between casein (non-reversible) and albumin (reversible) is 3·02 : 0·53, whilst in *human milk* this relation is 0·75 : 1·00; in human milk, then, there is abundance of albumin (reversible) and the coagulability is eight times less than with cows' milk. These relations explain the different nutritive effects of the two milks on infants.

Boiled milk may be distinguished from raw milk as it no longer contains reductase or catalase (*see* p. 135); also oxidation of the whey with a little hydrogen peroxide and treatment with pyramidone at 60° yields, with raw milk, a violet coloration, while that of boiled milk gives no coloration. The sugar and, partly, the salts are found in the aqueous solution composing the whey. Milk has an acid and an alkaline reaction (*amphoteric reaction*) at the same time, owing to the presence of primary (acid) and secondary (alkaline) phosphates. The natural acidity of milk is due, not to lactic acid, but to phosphates, carbon dioxide, citric acid, etc. Milk is alkaline to methyl orange and acid to phenolphthalein; lactic acid acts on methyl orange only when it has precipitated the casein and transformed the dicalcium phosphate into monocalcium phosphate (Bordas and Touplain, 1911). Urea, dicyandiamide, amino-acids, polypeptides, urethane, albumoses, xanthine bases, albuminoids, etc., are also amphoteric in reaction.

Milk changes very readily and, especially in hot weather, becomes acid and coagulates in a few hours. It keeps sound longer if cooled, boiled, sterilised or pasteurised, and then kept in hermetically sealed vessels; to prevent separation of the fat from the milk, the latter is first passed under great pressure through capillary orifices so as to rupture the fat globules. The sterilisation of milk by means of ozone has been suggested, but this is impracticable, since ozone acts quantitatively on the fat, forming ozonides which readily decompose, giving free fatty acids. Sterilisation by ultra-violet rays is incomplete and alters the composition and taste of the milk to some extent.

From milk defatted by centrifugation (*skim-milk*, containing less than 0·3 per cent. of fat), casein for making cheese and for industrial purposes is separated by addition of rennet (from the mucous membrane of the fourth stomach of young calves), which induces clotting owing to the enzyme it contains. Coagulation, with formation of lactic acid (increase from 3° to 15° of acidity), is also caused spontaneously in 24 to 48 hours by adding a dilute acid and keeping at 55° to 60°; the casein probably exists as calcium salt (1·55 per cent. CaO), which is decomposed by acids, the increase in the amount of soluble calcium salts favouring the separation of the casein. This casein, separated in the hot and pressed, gradually undergoes fermentation and conversion into Cheese. The latter may be either whole-milk cheese or *filled cheese*, prepared from milk the fat of which has been partially or completely removed and replaced by margarine. Copper vessels turn the cheese green on exposure to the air, and to avoid this, all the operations are carried out in vessels of wood, zinc, tinplate, or tinned copper (Besana), although, according to Fascetti, traces of dissolved copper are advantageous in cheese since they retard lactic fermentation; the latter author suggests, however, the addition of hydrogen peroxide, which has the advantages of the copper without its disadvantages. To avoid secondary fermentations

which separate at the surface on standing, or, better, on centrifugation in a separator of the *de Laval* type (Fig. 265).

After filtration through cotton-wool or, better, after a brief centrifugation to remove

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during maturation and prevent the swelling and spoiling of the cheese—which otherwise frequently occur—certain selected ferments are initially added under favourable conditions (Gorini, 1905), or attention is paid (Soncini, 1910) to the chemical surroundings in which maturation takes place (*see* p. 151).

After the cheese has been separated from the skim-milk, further boiling and coagulation of the latter yield the dissolved albumin (*ricotta*), the whey finally remaining being used either as food for calves or pigs or for the manufacture of *milk-sugar* (*see later*, Lactose). Skim-milk is used in some countries for the preparation of cheap and highly nutritious bread or of *kephir* (*see* p. 191), while in recent years it has been utilised for making milk-powder by evaporating it rapidly on a large rotating cylinder of metal heated by steam at 147° and in some cases enclosed in an evacuated chamber. A knife is arranged to detach the dry powder, which falls into a box. The milk may also be concentrated to some extent *in vacuo* and then either pulverised with hot air at 150° or passed in a thin film on to two revolving drums heated internally by hot water at 48°, the dried crust being scraped off, dried in a vacuum and powdered.

In some cases the water is removed from the milk by freezing and continual stirring, the residue being subsequently dried. Being deprived of fat, this powder does not become rancid, and if a little calcium saccharate is added, it dissolves and gives skim-milk on dilution with water. Milk-powder is also used by pastrycooks. When casein is to be separated for industrial purposes, it is obtained pure by treating the skim-milk at 50° to 60° with a current of sulphur dioxide (Soncini and Todtenhaupt, Ger. Pat. 184,300); it is dried in a stream of hot air or, to obtain it in a more soluble state, in a vacuum, while, if a highly pure product is required, it is dissolved in alkali and reprecipitated with nitric acid (it then has the percentage composition: C, 52·96; H, 7·30; N, 15·60; O, 22·54; S, 0·76; P, 0·84). Besides being soluble in alkalis and borax, casein dissolves in solutions of potassium iodide, sodium thiocyanate, sodium phosphate, etc. When dry and powdered, it may be used for certain concentrated food products (*plasmon*, *nutrose*, *tropon*, *sanatogen*, *somatose*, etc.), either in conjunction with, or in place of, meat extracts and peptones. These concentrated foods are obtained by heating the powdered casein on a water-bath with alkali solution or hydrochloric acid, the latter being afterwards neutralised with sodium carbonate and the liquid filtered and concentrated in a vacuum. Casein serves also for dressing textiles and for making greased paper (rendering it soluble with sodium carbonate or borate) and material similar to bone or celluloid, by compressing it when hot and hardening it with formaldehyde; *gallalith* and *lactite* are made in this way.

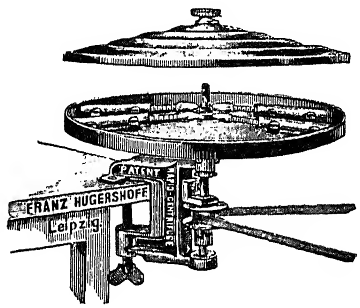

FIG. 266.

ANALYSIS OF MILK. Milk being a valuable nutrient for man, and being also easy to adulterate, it is usually analysed chemically to test its genuineness. Milk from cows of different breeds and districts varies within relatively narrow limits, but, in doubtful cases of adulteration, a mixture of the total milk of all the cows of the herd from which the suspected sample is furnished is also analysed. The *specific gravity* is measured with a hydrometer or a Westphal balance at 15° (*see* Vol. I., p. 76); for natural milk it varies between 1·0295 and 1·0335, and for separated milk between 1·033 and 1·036, while if much water has been added it is below 1·0295. The value of the specific gravity is not sufficient to prove watering, as this value is sometimes maintained unchanged by simultaneous removal of cream and addition of water. In such a case, use may be made of the *specific gravity of the whey*, which is never less than 1·027 with pure milk. Watering, even to the extent of only 5 per cent., is also readily detectable by the cryoscopic method examined in 1898 by G. Cornalba (for fresh, non-acid milks free from antiseptics, the cryoscopic point varies from 0·54 to 0·56) or by observing the whey in the Zeiss butyro-refractometer (*see* p. 463). The latter method was proposed recently by Ackermann, who prepares the whey rapidly by clotting 30 c.c. of milk with 0·25 c.c. of a calcium chloride solution of sp. gr. 1·1375, heating for 15 minutes on the water-bath, cooling to 17·5° and separating the serum by decantation; the reading on the Zeiss scale is 38·8 to 40 for pure milk, 37·7 for milk + 5 per cent. of water, 36·7 with 10 per cent., 34·8 with 20 per cent., 33·3 with 30 per cent. 32 with 40 per cent., etc. G. Cornalba (1908) holds that genuine milk contains at least 6 per cent. of *soluble substances* (*i.e.* dry residue less fat and casein), every 0·2 per cent. less than this amount indicating 5 per cent. of added water. Since natural milk does not contain nitrates, which are, however, present in nearly all waters, *watering* may also be detected by testing the milk for nitrates in the same way as wine is tested. Watered milk appears slightly blue when compared with genuine milk.

Comanducci and Frontera (1912) detect watering by means of the rotatory power of the whey in a 10 cm. tube at 15°; for pure milk this is 2·38° to 2·48°, whilst milk with 10 per cent., 30 per cent. and 60 per cent. of added water shows respectively 2·31°, 1·50° and 0·58°.

The *total residue* and *ash* are determined by evaporating 5 grms. of milk with a drop of acetic acid in a platinum dish, drying in an oven at 105°, and weighing; the dry residue thus obtained is then heated to redness until completely incinerated, and weighed; the ash is used for the detection of borax or sodium bicarbonate.

suspended impurities, the milk passes, while still tepid, to the chamber of the centrifuge, A, mounted on the axle, S, actuated by a pulley which is not shown in the figure (265) and which rotates several thousands (6 to 7) of times per minute. In this manner the skim-milk is expelled to the periphery and carried off by the tube, b, into the collecting plate, Bc, whilst the lighter cream rises and is discharged by the channel, e, into the collector, Cf. These separators easily treat 10 hectols. of milk per hour. The cream that separates is agglomerated into small lumps of butter by churning (*see*, for instance, Fig. 262), kneading, and so on, just as with margarine. To obtain a butter that will keep, however, the cream is subjected to pasteurisation and acidification (*see* Note on p. 472), the butter being worked with water that has been sterilised, for instance, by ozone or ultra-violet rays. The flavour of butter, which was formerly regarded as due to the esterification of the fatty acids, seems to result from the fermentation of lactose and the formation of aldehydes.

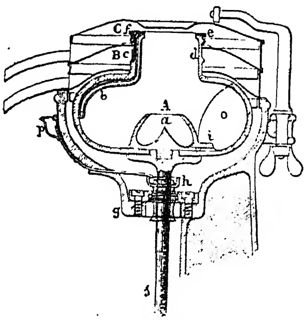

FIG. 265.

The percentages of the various fatty acids entering into the composition of the glycerides of butter are as follow stearic, 7 to 11; palmitic, 14 to 18; myristic, 11 or more; lauric, 14 to 16; oleic, 25 to 30; higher unsaturated acids, 4 to 5·7; also the volatile acids, butyric, caproic, caprylic, and capric; further, small proportions of acetic, arachic, and hydroxy-acids, cholesterol, phytosterol, lecithin, and a yellow colouring-matter; winter butter is less yellow than that of summer (green feeding of the cows). Unlike other fats, butter contains a mixed palmito-oleo-butyric glyceride, $C_3H_5(C_{16}H_{31}O_2)(C_{18}H_{33}O_2)(C_4H_7O_2)$.

Also, in comparison with all other fats, butter contains a large quantity of volatile acids soluble in water. The mean percentage composition of natural butter is: water, 15; fatty substances, 83; lactose, 0·5; proteins, 0·7; and mineral salts, 0·5.

Commercial butter should contain not less than 82 per cent. of fat, the remainder consisting of water, about 16 per cent., and salt, 2 per cent.

In judging the purity of butter, an examination is made of the butter fat obtained by heating the butter to about 50° and then leaving it to clarify and to deposit the water salts, etc. The constants for this fat are compared with those given in the Table on p. 466, attention being paid to the remarks on pp. 460 and 463 referring to the soluble volatile acids and to the butyro-refractometric reading, which should have the following values at different temperatures: 41·5 at 45°, 43·6 at 43°, 43·7 at 41°, 44·7 at 39°, 45·9 at 37°, 47 at 35°, 48·1 at 33°, 49·2 at 31°, 50·3 at 29°, 51·4 at 27°, and 52·5 at 25°.

Genuine milk has not less than 12 per cent. of dry residue, or, subtracting the amount of fat, not less than 9 per cent. The dry residue (r) may also be calculated from the specific gravity (s) and the percentageof fat (g) by Fleischmann's formula: $r = 1{\cdot}2g + 2{\cdot}665\,\frac{100s - 100}{s}$.

Determination of Fat. This is usually made with the *Gerber butyrometer* (Fig. 266). Into a special wide-mouthed flask with a long, narrow, graduated neck are pipetted 10 c.c. of concentrated sulphuric acid (sp. gr. 1·825), 1 c.c. of amyl alcohol, and 11 c.c. of milk, which are allowed to flow gently down the side. The flask is then tightly closed with a rubber stopper, wrapped in a cloth and shaken rapidly and vigorously; the flask with the pink or red liquid is immersed for six or seven minutes in a water-bath at 65° to 70° and then centrifuged on a flat plate, being arranged radially in clips with the mouth towards the circumference. After a few minutes centrifugation, the fat is separated from the acid casein solution and the percentage of fat by weight is read off on the graduated neck of the flask after the latter has been left for a few minutes on the water-bath.

The official method—which is used rarely and only in cases of dispute—of estimating fat is that of Soxhlet, and is based on the density of the ethereal solution of the fat extracted from the milk after rendering alkaline. In nearly all countries in has been established that a natural milk, obtained by milking completely a number of cows, contains as a rule not less than 3 per cent. of fat, in very rare cases 2·9 per cent., and more frequently 3·5 per cent.

If the specific gravity (s) and the dry residue (r) of a milk are known, the fat (g) that it should contain is deduced from Fleischmann's formula: $g = 0{\cdot}833r - \frac{2{\cdot}22\,(100s - 100)}{s}$. To calculate the dry residue (r) of a whole milk use may be made of Fleischmann's corrected formula: $r = 1{\cdot}2g + \frac{2{\cdot}665\,(100s - 100)}{s}$, while that of a skim-milk is given by: $r' = 0{\cdot}2g + \frac{2{\cdot}665\,(100s - 100)}{s}$

The most certain method of detecting adulteration of butter with *coconut oil* is by determining the volatile fatty acids *insoluble in water* (Polenske number),[1] and for other adulterations various tests are made.

The *degree of rancidity* is determined as described on pp. 463 and 464.

In order to avoid rancidity, butter must be kept or despatched in ice or in cold chambers. Butter may be coloured yellow by saffron, turmeric or, more commonly, *annatto*, which is an extract of the fruit of *Bixa orellana* made into a paste with an oil; the use of coal-tar dyes is prohibited.

Renovated butter is prepared in America from rancid butter, which is kneaded with a solution of sodium bicarbonate (*e.g.* in the Werner and Pfleiderer kneading machine, Fig. 264, p. 473), and is then washed with just tepid water in the rotating-plate kneader (Fig. 263, p. 472) until it no longer gives an alkaline reaction. It is then kneaded again in the former machine with milk, cooled with a jet of very cold water and treated like ordinary butter a second time in the latter kneader. Natural butter can be distinguished from renovated butter since when melted at a moderate temperature, the former gives a limpid and the latter a turbid mass.

BONE FAT is obtained mainly from glue factories, and is extracted from the crushed bones either by boiling with water (*see* Vol. I., p. 647) and skimming the fat which collects at the surface, or by treatment with benzine or carbon disulphide in an extraction apparatus (*see later*). The first method yields 3 to 4 per cent. of fat, and the second 7 to 9 per cent. The latter has, however, an unpleasant smell and is dark and of inferior quality; it may be refined by means of dilute sulphuric acid or sulphuric acid and dichromate or barium peroxide (*see* Tallow). Its constants are given in the Table on p. 466.

It is used in making soap, especially resin-soap, and also candles and cart-grease.

[1] Polenske (1904) showed that coconut oil contains a high and constant proportion of volatile fatty acid *insoluble in water*, whilst butter contains very little of these. If the Polenske number (or *new butter-value*) is expressed in c.c. of decinormal KOH necessary to neutralise the insoluble volatile acids contained in 5 grms. of the fat, its value is 16·8 to 17·8 for coconut oil and 1·5 to 3 for pure butter. The Reichert-Meissl-Wollny number and the Polenske number may be determined by a single operation, the butter being saponified in the following manner (Leffmann and Beam): 5 grms. of the filtered butter, together with 20 grms. of glycerine and 2 c.c. of caustic soda solution (100 NaOH to 100 H_2O), are placed in a flask of about 300 c.c. capacity, this being heated with a naked flame. After 5 to 8 minutes' boiling, the water evaporates, frothing ceases, and the mixture becomes clear, the heating being then continued for a few minutes longer. When the liquid has cooled to 80° to 90°, 90 c.c. of water at 80° are added, a clear and almost colourless solution of the soap formed being thus obtained. To this solution, heated nearly to boiling, are added 50 c.c. of dilute sulphuric acid (25 c.c. of the concentrated acid in a litre) and ½ grm. of powdered pumice, the volatile acids being then distilled so that 110 c.c. is collected in 19 to 21 minutes in an apparatus corresponding exactly with that shown in Fig. 254 on p. 461.

The 110 c.c. flask is cooled in water at 15° and inverted several times to cause the drops of insoluble fatty acids to collect. The liquid is filtered, titration of 100 c.c. of the filtrate with decinormal KOH giving the Reichert-Meissl-Wollny number. The tube of the condenser and the 110 c.c. flask are then washed with three separate amounts of 15 c.c. of water, which is passed through the filter, the flask being subsequently washed with three quantities, each of 15 c.cc. of neutralised 90 per cent. alcohol. Titration of the whole of the alcoholic filtrate with decinormal KOH gives the Polenske number, which allows of the detection of 10 per cent. of coconut oil in butter. The result has been stated to be inconclusive if the cows have been fed with coconut cake.

Adulteration with *margarine* is readily detected by the content of aggregated crystals which are observed under the microscope in polarised light or, better, in light which has previously passed through a selenite plate. Fresh, non-melted butter does not, indeed, yield crystals, but old and rancid or melted butter does give them, so that, in this case, the test is invalid.

The determination of *water*, fat, solids not fat (casein, lactose, and mineral salts) can be simply carried out, according to Fahrion (1906), as follows: in a platinum crucible, tared together with a glass rod, are weighed 2·5 to 3 grms. of butter, which is then heated over a small flame and stirred until it is melted and clear; reweighing gives the proportion of water. The residue is then dissolved in light petroleum and the solution filtered through a tared filter, which is well washed with solvent. The filtrate is distilled in a tared flask and the remaining fat dried for an hour in an oven at 100° to 102° and weighed. After drying at 100° the weight of the filter less the tare gives the non-fat. By burning the filter in the crucible, incinerating and weighing, the salts (NaCl) or mineral substances are obtained.

No addition of antiseptic, for the keeping of butter, is allowed; boric and salicylic acids can be detected as in beer. The presence of formaldehyde may be ascertained by distilling 25 c.c. of water in a current of steam from a flask containing 50 grms. of butter and 50 c.c. of boiling water; the distillate is tested by means of Rimini's reaction (*see* p. 131).

Addition of artificial yellow colouring-matter is shown by the intense coloration assumed by absolute alcohol when shaken with the fused butter.

HOG'S FAT (Lard) is obtained by melting the fatty parts of the pig, as in the case of tallow (Refining, *see* p. 470). In Germany large quantities of it are consumed for culinary purposes, and in Italy almost the whole of this product is used by the lower classes as a substitute for butter and oil. Considerable amounts are employed in making soap and candles. In 1891 Germany imported 75,000 tons from the United States, but since this was prepared with all the refuse of oxen and pigs, and also with the residues of diseased animals, while addition of appreciable quantities of cottonseed oil and bleaching by the addition of lard stearine were also resorted to, the food-value was greatly lowered. The Table on p. 466 give its constants. The presence of cottonseed oil is detected by Halphen's test (*see* p. 470).

In the United States the production of lard is continually increasing, 21 millions of pigs being killed in 1902 and 25½ millions in 1905, the exports amounted to 250,000 tons (£10,800,000) in 1911.

FISH OILS: WHALE OIL and COD-LIVER OIL. The fat of the whale, seal, and dolphin is extracted from a species of lard contained in the membranes of the brain and back; it is, however, worked in a primitive manner, being left to melt and putrefy in barrels exposed to the sun. The oil being thus separated, the residue is boiled with water to extract the tallow. When heated with water, the oil loses its unpleasant odour to some extent.

The head and other parts of the body of certain whales, especially *Physeter macrocephalus* (Cachelot whale), contain an oil already separated and different from that of the lard; it solidifies at the ordinary temperature, giving the so-called **SPERMACETI** (or **Sperm Oil**), which, after filtration, pressure (to separate the stearin or solid wax), boiling with water and a little caustic soda and repeated washing with water, forms a fat or oil of great value in the manufacture of pharmaceutical products, perfumes, and high-class candles.

Cod-liver Oil (from the fresh liver of *Gadus morrhua*, caught in large numbers in Norway and elsewhere) is used in considerable quantities as a recuperative medicine in virtue of the small proportion of chemically combined iodine and of the large amounts of readily emulsifiable fatty acids it contains. It is now obtained with a less unpleasant taste and smell, as it is being prepared in a more rational way by melting it in closed vessels with hot water or direct steam, the best results being obtained in absence of air—in an atmosphere of hydrogen or carbon dioxide or in a vacuum (Eng. Pat. 25,683, 1906).

Natural cod-liver oil, prepared by the old process, has a considerably higher acidity (acid number, 8 to 25) than that separated by the more modern methods (acid number, 0·7 to 1·4).

The production of cod-liver oil in Norway shows a continual increase, although it varies in different years, according to the abundance or scarcity of the fish. from 20,000 to 100,000 tons per annum, about one-half of this amount being obtained by the newer methods of extraction.

Adulteration of the oil is detected by analysis, taking account of the constants given in the Table on p. 466.

Fish-oil Waste consists of inferior oils of unpleasant odour and taste, the odour being due especially to an unsaturated compound, *clupanodonic acid*, $C_{18}H_{28}O_2$, which combines with 8H to form stearic acid. These oils are used in dressing leather, in the manufacture of **DÉGRAS**,[1] also employed for treating skins, and in the preparation of fatty acids for soap-

[1] **DÉGRAS** is obtained in the *chamoising* process (separation of the fat from the skins after it has served to oil them during tanning) and is used for tanning other skins. It consists essentially of water (30 to 40 per cent.), rancid fish oil, resinous substances (*dégragène* or *dégras-former*, 14 to 20 per cent.) from the oxidation of the oil, mineral substances (about 2 per cent. consisting of lime, soda, and sulphates) and residues of skin, membranes, hair, etc. (about 5 per cent.). It has an acidity number of 25 to 35, an iodine number of 34 to 36, a saponification number of 144 to 155, an acetyl number of 32 to 44, and 1 to 3 per cent. of non-saponifiable substances. It is yellowish brown, has an odour of fish oil and readily forms a very persistent emulsion with water. *Dégragène* is the characteristic constituent and, unlike other resins, is insoluble in light petroleum.

Its value in dressing skins lies in its property of penetrating readily, and in large quantities the *semi-moist* skins, in the pores of which it becomes uniformly distributed, imparting very desirable softness and fullness, as well as keeping qualities.

This use of dégras has been known for many years and has increased so rapidly that the supply is no longer sufficient, factories for making *artificial dégras* having been established. This is prepared by kneading refuse and clippings of skins with fish oil, exposing the mass to the air to oxidise and pressing out the artificial dégras or *moëllon:* the residue is then treated with a

these fatty acids are *deodorised* by heating with 15 to 20 per cent. of concen- .phuric acid at 30° to 40°, washing and distilling with superheated steam. Suc- tempts have been made to harden these oils by hydrogenation (*see* p. 480). In n 1913 a single factory treated daily 150 tons of these oils with 4500 cu. metres lytic hydrogen.

FAT. Pliny mentions the use of this fat in medicine, and its employment for ose extended to the seventeenth century. In 1856 Chevreul classified it with the ing to its richness in cholesterol, and in 1867 Vohl proposed its preparation from -waters of wool. When washed with tepid water, soap, and a little potassium or m carbonate, certain greasy wools (from Australia) lose as much as 40 to 50 per their weight as soil, fatty acids, potash soapy substances and fat, secreted by the l cells of the skin. The wool from certain races of sheep may contain from 7 to 35 of true fat (if the sheep are not washed before shearing).

me factories the wool fat is extracted from the dried wool by means of carbon le or, better, of benzine (at Verviers, in Belgium, the wool from all the establish- the city has for several years been washed with benzine in a large works), subse- ashing with water and a little soap being then more easy and economical. The obtained in this way after distillation of the solvent is slightly coloured and almost n water, and is ready for the market. Usually, however, the dirty wool is washed eviathan machine, the soapy, greasy wash-waters being first allowed to stand to earthy matters and then treated with dilute milk of lime or, better, with calcium solution slightly acidified with hydrochloric acid. The soaps and fatty acids c, cerotic, a little caproic and oleic and traces of stearic, isovaleric, butyric, myristic, ic, and lanoceric) are precipitated as calcium salts and carry down the *wool fat,* s only slightly saponifiable owing to its large content (55 to 60 per cent.) of rol, isocholesterol, ceryl alcohol, lanolyl alcohol ($C_{12}H_{24}O$) and carnaubyl alcohol O), which do not contain glycerides. After this treatment the wash-waters are eft to stand or coarsely filtered to separate the pasty mass ; in some cases the water ved from the calcium soap and fat by centrifuging in a separator similar to that milk (Fig. 265, p. 476). The paste thus obtained is *dried* in the sun or in an oven n made into cakes with sawdust, etc., the rather dark *crude wool fat* being extracted ese by means of carbon disulphide or, better, benzine. The residue from the cakes. reated with dilute sulphuric acid, yields fatty acids, and the resultant aqueous n, coarsely filtered to remove solid substances, deposits the fatty acids when heated. s obtained, wool fat is dirty yellow, transparent, and very viscous (it can be obtained llow by special refining processes) ; it melts at 35° to 40°, and has the saponification r 85 to 105, the iodine number 13 to 17, the acid number 0·5 to 1·3, the Hehner r 85 to 95, the Reichert-Meissl number 6 to 7, and 0·5 to 1 per cent. of water, while tory power in saccharimetric degrees is + 10·2 to + 11·2. Commercial lanoline ot contain more than 30 per cent. of water.

ol fat is better suited than any other fat or even vaseline as a basis for salves and nts, and has also considerable power to penetrate the skin. It mixes readily with roportions (up to 105 per cent.) of water (which separates in the hot) and, if mixed) per cent. of olive oil, it can absorb 320 per cent. of water.

some cases the crude wool fat is distilled with superheated steam, this procedure a *wool oil* or *wool oleine* containing 40 to 50 per cent. of fatty acids, 35 to 45 per

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uantity of fish oil, this operation being repeated until practically no residue remains. ots have also been made to obtain moëllon by pulverising fish oil in the air at 120° and ying with water. At the present time, the term *dégras* is applied to a complex substance ssing skins and consisting of a mixture of moëllon with wool fat, tallow, and other solid hilst by moëllon is indicated the aqueous emulsion of oxidised fish oil. Artificial dégras preferred to the natural product, since different types can be prepared for different purposes, ypes being of more constant composition, and hence more certain in their effects. A good al dégras usually contains 15 per cent. or more of dégragène and less than 20 per cent. er. When such dégras contains more than 1 to 2 per cent. of non-saponifiable substances, re derived, not from the fish oil, but rather from the wool fat, resin oil, mineral oil, etc. dégras sometimes contains 1 to 2 per cent. of soap and as much as 5 to 6 per cent. of ores : in general, it should contain less than 0·05 per cent. of iron and, when spread in a yer on glass and kept for 10 hours in an oven at 100°, it should not form a varnish, but . assume only a horny consistency. When smeared on moist and well-pressed paper, ıld be absorbed within an hour, leaving only a minimum residue.

tural dégras costs about 28*s*. per cwt., the artificial product of the first quality about 20*s*., e French (moëllon) about 34*s*.

cent. of hydrocarbons, and 5 to 10 per cent. of alcohols, while the distillate deposits a *wool stearine*, which melts at 42° to 55°, has the iodine number 37, and the saponification number 170, and contains cholesterol and, altogether, 73 to 88 per cent. of free, solid fatty acids.

In 1905 Germany exported 134 tons (130 in 1903) of lanoline, of the value £10,000.

CHRYSALIS OIL. The dead silkworm chrysalides remaining after removal of the silk from the cocoon contain 25 to 27 per cent. of oil recoverable by pressure or extraction by solvents. The oil is reddish-brown and of somewhat unpleasant odour, deposits stearine at the ordinary temperature and sets to a buttery mass at 0°. Its iodine number is 112 to 118, and its saponification number 190 to 195, and its fatty acids melt at 32° to 36° and solidify at 28° to 30°. The oil contains up to 30 per cent. of free fatty acids and may be decolorised with fuller's earth. The chrysalides were formerly used directly as a nitrogenous fertiliser (7 to 8 per cent. N), but, nowadays, the oil is first extracted, the residue, containing 10 to 12 per cent. of organic nitrogen, being used as a fertiliser. The crude oil was utilised partly for making inferior, odorous soaps, and also for the separation of the fatty acids. After distillation in a vacuum the oil gives hard, odourless, fatty acids (Molinari and Fachini, 1907).

Tsujimoto (1914) deodorises and decolorises chrysalis oil by shaking it for an hour with 6 to 8 per cent. of 50 per cent. sulphuric acid at 100°, then washing it well with water and treating it at 130° with 15 to 20 per cent. of *Kambara earth* (a Japanese earth superior to Florida earth ; *see* Vol. I., p. 738). Thus prepared, the oil yields consistent fats on hydrogenation (*vide infra*).

Italy produces about 50,000 tons of fresh cocoons, giving about 15,000 tons of air-dried chrysalides, from which at least 3000 to 3500 tons of crude oil is obtainable.

INDUSTRIAL HARDENING OF OILS BY MEANS OF HYDROGEN

Glycerides of unsaturated fatty acids (oleic, linolic, linoleic, etc.) preponderate in ordinary liquid oils and fats, and those of saturated fatty acids in ordinary solid fats, which are largely used as fatty foods and for making soap and candles. Large quantities of certain oils are, therefore, converted into solid fats which are of higher value and more readily utilisable (*see* note 1, p. 359).

Although various hydrogenation processes had been known in the laboratory, industrial application of these to the hardening of oils was not attempted until after the work of Sabatier and Senderens on the hydrogenation of organic compounds in general (*see* pp. 35, 67, 124). On the basis of these investigations, Normann (Ger. Pat. 141,029, 1902) first applied hydrogenation to unsaturated fatty acids and glycerides (oils). The process was not, however, at once applied on an industrial scale in Germany, but was used first in England by Crosfield and Sons, of Warrington, and also in Holland ; only in 1911 was it utilised in Germany, finely divided nickel being employed as catalyst.

Better results are obtainable with finely divided *palladium*, which works at 80° to 90° (in 1908, Paal used colloidal palladium at almost the ordinary temperature), but, although a large part of the palladium (which serves for a long time and is not so sensitive as nickel to poisons such as sulphur, H_2S, CS_2, Cl, organic thio-compounds, hydrocarbons, etc.) is recoverable, it is, nevertheless, very expensive. Palladium chloride, which Skita proposed to use at a pressure of 2 to 3 atmos., is cheaper, and at 100° one part of palladium suffices for 100,000 parts of oil.

The nickel catalyst is prepared by reducing the oxide obtained either by calcining the nitrate or by precipitating the sulphate by means of an alkali, the oxide being deposited on an inactive, porous support such as pumice, coke, asbestos, etc., and then reduced by hydrogen at about 300°. The active, finely subdivided nickel thus obtained completely hydrogenates oil at temperatures below 150°. Decomposition of nickel tetracarbonyl (*see* Vol. I., p. 846) also yields an active product.

When prepared in this way, the catalyst is emulsified with the oil. The oxide itself may be mixed with some of the oil and then reduced by hydrogen in a jacketed autoclave at 230° to 240° for two hours ; the emulsified catalyst thus formed is mixed with the oil to be hardened, a temperature of 120° to 160° being sufficient for this operation.

Bedford and Erdmann (Ger. Pat. 292,649, granted in 1916 in spite of opposition from Normann) applied to unsaturated fatty acids the methods developed in 1907 to 1909 by Ipatiev and in 1910 by Wilbuschewitsch (who effected catalytic hydrogenation of organic

substances in the hot at pressures of 8 to 10 atmos. by means of nickel). Erdmann used apparatus of copper or aluminium, which may, however, influence the taste and odour of the product. Wimmer and Higgins use as catalyst nickel lactate, acetate or formate, the action of which is improved by addition of carbon; nickel borate has also been used. Nickel oxide has a slow action and hardens oils at temperatures above 200° to 240°, the oil being darkened. Erdmann considers the catalytic action of the oxide as due to the alternate formation of the oxide and suboxide, but others suppose that the oxides are reduced by the hydrogen to nickel, to which the true catalytic effect is due.

A diagram of the plant proposed by Wilbuschewitsch (Eng. Pat. 30,014, December 10th, 1910) for use in the preparation of the catalyst, and in the hardening of the oils, is shown in Fig. 267. The highly active nickel catalyst is obtained by soaking burnt clay in sulphuric acid, then in nickel sulphate solution, and afterwards in sodium carbonate solution, the nickel carbonate thus formed being converted by heating into the oxide and this into nickel by the hydrogen. The finely powdered mass is readily oxidisable and is emulsified directly with oil and kept. In *R* is placed the oil to be treated and in *O* the catalyst, the two liquids being drawn by the pumps, *A* and A_1, in the proper proportions to be emulsified in *B* and passed through the pipe, *G*, and distributed by the valve, *H*, and the pulveriser, *C*, to the jacketed autoclaves, J_1, J_2, etc. The hydrogen is injected by a compresser, *K*, at a

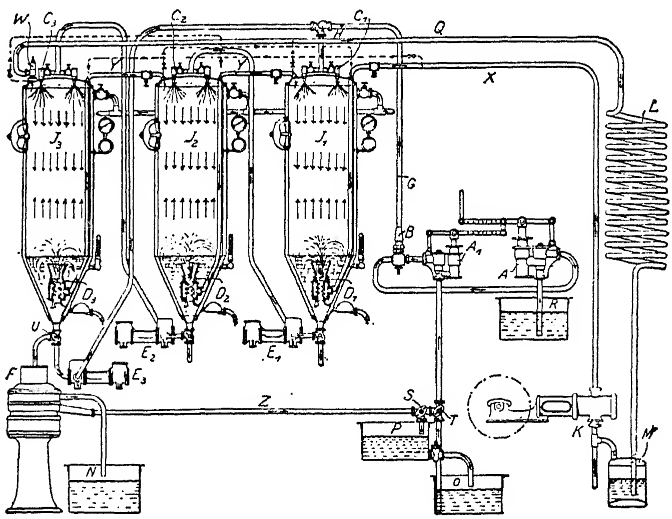

FIG. 267.

pressure of 9 atmos. through the tube, *X*, to the bottom of the autoclave, where it is finely subdivided by the distributors, D_1, D_2, D_3. The autoclave is heated first to 100° to 160°, according to the kind of oil, the partly reduced oil collecting in the conical base of J_1 being drawn off by the pump, *E*, and injected into J_2, while the hydrogen escaping from J_1 passes into J_2 through the pipe, *Y*; the oil then goes through the pump E_2 to J_3. In the passage of the oil through each autoclave, the melting-point is raised by about 15°, and when the desired melting-point has been reached, the oil is discharged through the cock, *U*, into the centrifugal separator, *F*, the solidified oil being separated in *N*, while the oil containing the catalyst passes through the pipe, *Z*, and the cocks, *S* and *T*, to be circulated again in the autoclaves. As the catalyst becomes exhausted the amount used is increased (1 per cent. of the fresh material suffices), being discharged into *P* when almost completely exhausted. On the other hand, the hydrogen not absorbed in the last autoclave, J_3, issues from the valve, *W*, and through the tube, *Q*, to the cooling coil, *L*, and thence to the washer, *M* (containing sodium carbonate), from which it returns to the cycle through the compressor, *K*. The reduction generates heat and the temperature in the autoclaves is sometimes regulated by passing cold water through the jackets.

The amount of hydrogen required varies with the nature of the oil and the degree of hydrogenation required, and is usually 8 to 12 cu. metres per 100 kilos of the oil. The hydrogen from water gas should, after purification, contain less than 2 per cent. of CO and

less than 0·1 per cent. of H_2S (*see* Vol. I., p. 141). The rapidity of the reaction and the life of the catalyst increase with the purity of the gas.

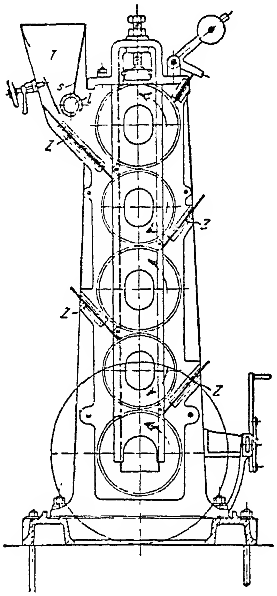

FIG. 268.

The iodine number of all hardened oils is very low (5 to 25). The cholesterols and phytosterols undergo no change and serve to indicate if the original oil was a mixture of vegetable and animal oils. Hydrogenation is applied to inferior oils (olive, cottonseed, fish, etc.) to obtain consistent fats for making margarine and candles. In general, oils thus treated lose their original odour and assume that of tallow.

In Germany about 200 tons of hardened oils were produced per day in 1913, and during the European War the manufacture assumed enormous importance. In France two factories have an output of 20,000 tons per annum. Before the War the total cost of hydrogenation was calculated at £6 to £8 per ton of oil.

Hardened oils, sold under different names (*talgol, talghin, candelite, cruteolin*, etc.), have m.-pt. 38° to 50°, acid value 3·5 to 4, iodine number 20 to 60, saponification number 189 to 192, non-saponifiable substances 0·3 to 0·5. They give increased yields of soaps, but these form less lather and wash more slowly. The refractive index is lowered somewhat and the colour reactions are attenuated or annulled. Almost all of them retain minimum traces of catalyst, and nickel may be detected in the ash by means of dimethylglyoxime (*see* p. 398).

VEGETABLE OILS

In plants oils accumulate especially in the seeds and the fleshy parts of the fruit, rarely in the roots. The composition of these oily parts varies somewhat with the locality and with the character of the season.[1]

[1] **The Mean Compositions of Oily Seeds and Fruits** (the maxima and minima are 10 to 15 per cent. above and below the mean values) are as follows :—

	Water per cent.	Ash per cent.	Oil per cent.	Organic matter free from oil per cent.	Proteins in 100 parts of organic matter.	Cakes after pressing. Fat per cent.	Cakes after pressing. Protein per cent.
Olive : pulp	24·22	2·68	56·40	16·70	1·10		
kernel (shell)	4·20	4·16	5·75	85·89	2·50	5–15	4–8
seed	6·20	2·16	12·26	79·38	2·16		
Linseed : winter	8·65	3·15	35·20	53	22·10	6–8	30–38
summer	7·80	3·20	31·60	57·40	24		
Ricinus (seeds) : Italian	8	2·93	52·62	36·45	25·50	7–10	28–31
Indian	7·26	3·40	55·23	34·11	24·26		
Sesamé (seeds) : brown Levant	5·90	7·52	55·63	30·95	21·42	10–15	35–40
yellow Indian	7·06	6·85	50·84	35·25	22·30		
Cottonseed : Egyptian	7·54	8·60	23·95	59·91	27·20	12–16	36–48
American	8·12	9·44	20·58	61·86	28·12		
Colza or rape (seeds)	6	4·30	38	51·70	20	8–10	29–32
Ravison (seeds) : fresh	9·10	4·80	36·80	49·30	2·50		
two years old	5·25	4·36	39·25	51·14	4·20	7–10	29–32
Arachis (shelled nuts) : fresh	7·37	2·43	37·84	52·36	27·25		
old	2·75	2·50	41·63	53·12	27·85	6–9	44–50
Hempseed	8·65	3·45	33·60	54·30	15·95	8–12	28–33
Mustard : black	6·78	4·21	22·20	66·81	20·52	—	—
white	7	4·45	29·30	59·25	28·20	—	—
Poppy : white	8·85	3·42	55·62	32·11	16·89		
black	9·50	4	51·36	35·14	17·50	9–11	33–37
Sweet almonds	9·53	2·86	51·42	38·19	22·50	—	—
Maize : whole grain	—	—	6·10	—	—	—	—
germ	—	—	44·46	—	—	6–10	14–18
Palm fruit	—	—	65·72	—	—	—	—
Palm kernel	—	—	45·50	—	—	7–9	14–17
Coconut	—	—	45·63	—	—	10–14	18–22

The oil is extracted by two processes: *by pressure* and *by means of solvents*. Edible oils are always obtained by the former method, as also are most of the others, solvents being used to extract the remaining oil from the pressed residues (*oil-cake*), when these are not to be used for cattle-food.

According to the power and degree of perfection of the pressing appliances, from one-fourth to one-seventh of the total oil is left in the cake. Extraction of the powdered cake with solvents removes all but the fifteenth part of the total amount of oil (1 to 2 per cent. instead of 10 to 12 per cent.).

The seeds are not worked up immediately after gathering, but are first matured, dried, and turned in bins or silos. They are then cleaned with sieves

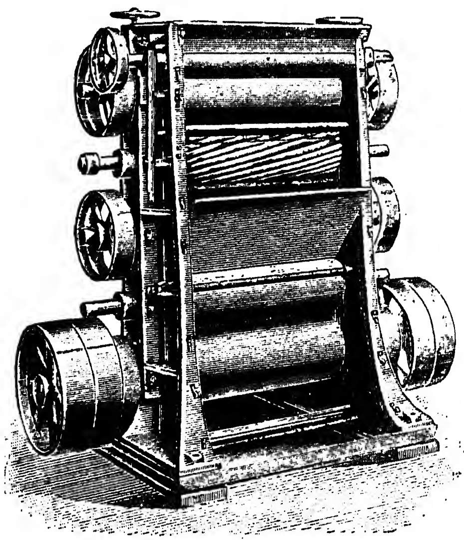

FIG. 269.

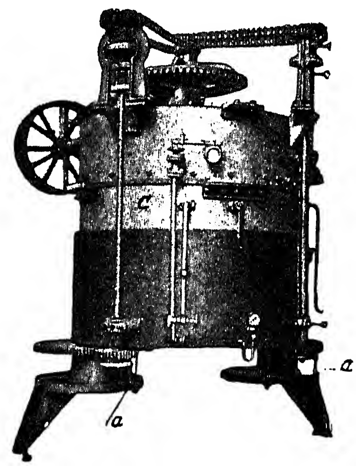

FIG. 270.

and fans, crushed in a kind of roller press (Figs. 268, 269) and powdered (sometimes this is done directly) in vertical cast-iron or stone mills like that illustrated in Fig. 185 on p. 269. A mill with a diameter of 1·7 metre converts about 35 litres of linseed into flour in twenty-five minutes.

To obtain the edible and so-called virgin oil, the flour is pressed cold, although more commonly the pressing is carried out in the hot, this increasing the yield but injuring the quality and colour. The flour is heated in the apparatus shown in Fig. 270, this being furnished with discharge orifices, *a*, which allow the quantity corresponding with each cake to be delivered. Steam heating is applied in the upper chamber, *c*, while the lower one, *b*, is well insulated so as to maintain the temperature of the mass.

Nowadays the pressing is effected almost everywhere with hydraulic presses of various forms,[1] and only in small works are wooden or metal screw-presses still employed.

[1] The **HYDRAULIC PRESS** is based on Pascal's principle, according to which a pressure exerted on any point of a liquid mass is transmitted with the same intensity in all directions. So that, if a pressure of 1 kilo is exerted, by means of a piston 1 sq. cm. in area, on a liquid in one arm of a U-tube, the other branch of which is closed by a piston 16 sq. cm. in area, this would require a pressure of 16 kilos to balance the first piston (Fig. 271), the pressure transmitted by the pressing surface being proportional to the area receiving the pressure.

The hydraulic press consists of a suction pump, *P* (Fig. 272), which draws water from the reservoir, *A*, and forces it through the strong copper tube, *t*, into the thick-walled chamber, *B*, hermetically sealed at the upper part by a large piston, *b*, carrying a wide plate, *c*, on which is placed the material to be compressed. The compressing surface is that of the base of the small pump-piston and the surface receiving the pressure is given by the base of the piston, *b*, the pressure received being dependent on the ratio of the sections of the pistons and on the

A hydraulic press which is widely used is the ring-press of Brück and Hübner, of Mannheim, shown in Fig. 275. The powdered seeds are placed on the rings, *a*, the base of which

ratio between the arms, *OP* and *PR*, of the pump-lever. If *PR* is ten times as long as *PO* and the force exerted at *R* is 30 kilos, the piston of the pump receives a pressure of 300 kilos (30 × 10); if, on the other hand, the section of the large piston, *b*, is fifteen times as great as that of the small piston, the pressure exerted on the former will be 4500 kilos (300 × 15).

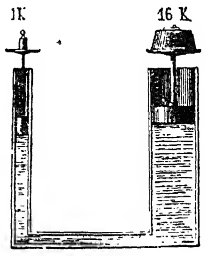

FIG. 271.

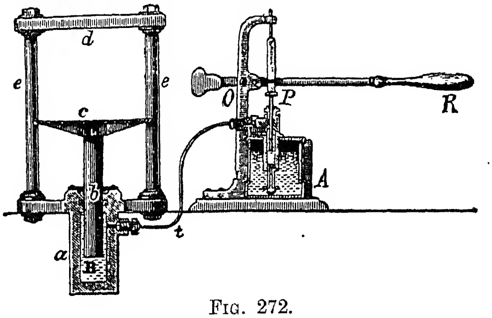

FIG. 272.

When the piston, *b*, rises, the plate presses the substance against a strong cover, *d*, fixed by three or four columns, *e*. When the pressure is to be released, the water is discharged from the chamber, *B*, and the piston descends. The pump is provided with a safety-valve which regulates the maximum pressure desired. The large piston is made tight by encircling it at *b* with a leather ring (devised by the Englishman Bramah) with an inverted U-section; the water, in its attempts to escape along the sides of the piston, enters the ring and forces its edges against the piston with a pressure increasing with the pressure of the water, and thus forms a true hermetic seal.

Nowadays horizontal hydraulic presses, which discharge the oil and cake more easily, are also used, but these occupy more space, while at the same time the piston does not recede of itself at the end of the operation.

In practice, when a substance is to be compressed with a hydraulic press, two or more pumps are used. The first, which has a long stroke, raises the piston and plate rapidly, since at first the resistance is small; when the pressure increases, the compression is continued more slowly by means of a small pump.

To avoid attention to a number of pumps and loss of energy, works employing many hydraulic presses make use of the so-called *hydraulic accumulators* (Armstrong, 1843), which provide a store of water under high pressure for the feeding of several presses at once (Figs. 273 and 274). A piston, *L*, moving in a cylinder, *B*, just as in an ordinary hydraulic press, receives pressure from below by means of compressed water from a pump, passing through *p* and v_1; the upper part of the piston is fixed to the centre of a plate, *C*, which, by means of three columns, *S*, supports the plate, *E*, carrying the heavy iron discs, *D*. When the piston is raised by the compressed water entering *A*, the whole accumulator, *E*, *C*, and the discs, *D*, are raised. When v_1 is closed *A* contains a store of water under great pressure which transmits pressure to a number of hydraulic presses simultaneously when the cock, v_2, communicating with these presses is opened. In order to prevent the piston, *L*, from being raised too much and so forced out of the cylinder, *B*, the lower part of the piston is provided with a small vertical channel with a lateral exit; when the latter is forced from the top of the cylinder, *B*, the water escapes, the pressure is lowered and the piston falls. Large works are supplied with two or more accumulators, so that when one is raised and the other at its low position excess of compressed water supplied by the pumps at any moment is directed to the latter accumulator, which is hence raised. In this way, also, the final pressure of the hydraulic press can be utilised before discharging it, energy that would otherwise be lost being thus saved.

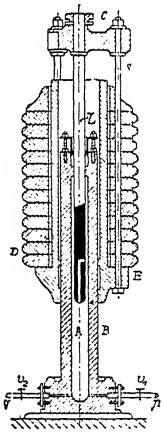

FIG. 273.

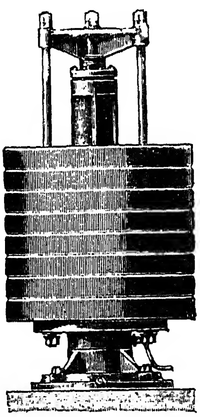

FIG. 274.

By these means, a uniform and persistent pressure may be exerted on several presses, but it is exerted, not gradually, but instantaneously, which may be disadvantageous in certain cases, unless indeed various accumulators at different pressures are employed. Accumulators with small pistons may be used for pressures up to 400 atmos. The circular iron rings composing the accumulator may be replaced by a single large cylinder filled with scrap iron or stones.

The pressure of a hydraulic accumulator may be exerted in some degree gradually by connecting it with a compressed-air chamber (*automatic accumulator*). As liquid for use in the accumulators, water, glycerine, or oil may be employed.

consists of a movable, perforated steel plate covered with a disc of woollen or horsehair material. The flour is well pressed by hand or by a suitable machine, covered with a second woollen or horsehair disc, and passed along the guides, *b*, being thus brought between two plates, *e*, which are smooth underneath and grooved on the top and fit exactly into the

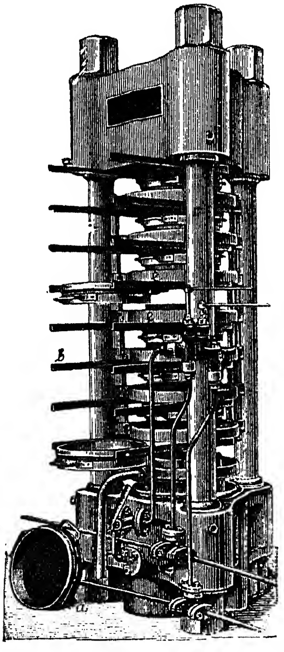

FIG. 275.

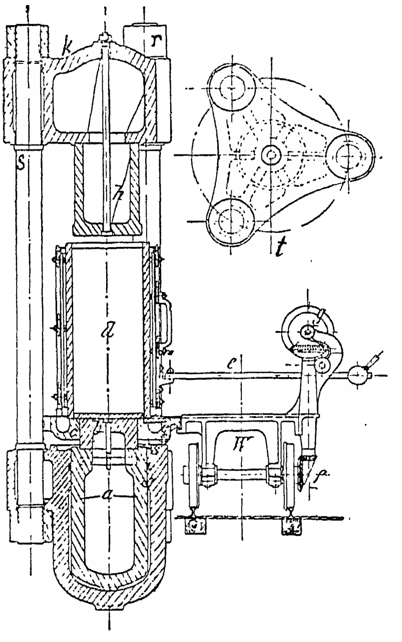

FIG. 276.

two rings containing the flour, one above and the other below. The grooved side of the plate has also a circular, peripheral channel which collects the oil issuing from the perforated base of each of the rings when the press is working.

The automatic changing of the rings requires one to two minutes, about the same length of time being occupied in discharging them, while, under a pressure of 200 to 300 atmos., the pressing is complete in eight to ten minutes. Especially with palm oil and coconut oil, the pressing may be carried out in the hot, the plates being arranged so that they can be heated; this procedure shortens the time of pressing and increases the yield of oil. In some cases the pressing is carried out first at a low pressure, which gives an oil of improved quality, the cake thus obtained being ground (*e.g.* by an Excelsior mill, p. 200) and squeezed under a high pressure for the extraction of a further quantity of oil of lower grade.

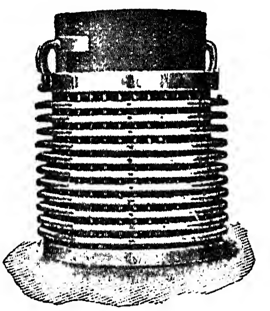

FIG. 277.

The presses most commonly used are of the type shown in Fig. 276 (in plan at *t*), *d* being a cylindrical cage made of a number of vertical steel bars fixed to stout horizontal rings surrounding them (Fig. 277), so as to leave vertical slits through which the oil flows. The cakes consisting of 2 to 3 kilos of the hot flour and well wrapped in strong horsehair material, are placed in *d*, the superposed cakes being separated by fluted steel discs. The pressure is raised gradually to 200 to 300 atmos. When batteries of several cages are used (Fig. 278) hydraulic accumulators (Figs. 273, 274) are often employed.

Double hydraulic presses are sometimes used (Fig. 279), the two cages being rotatab e round the column *s*. One cage is discharged and recharged while the pressure is acting on the other cage.

With the presses about 70 per cent. of the oil of seeds and fruits is extracted; by means of suitable solvents 98 to 99 per cent. may be obtained.

Extraction of the oil by means of solvents (first attempted in England in 1856), from the crushed seeds or broken cake, is effected with carbon disulphide (*see* Vol. I., p. 493)—which has considerable solvent action on fats, even in the cold, but also removes a certain amount of chlorophyll—or with light petroleum (benzine), which exerts its maximum solvent effect in the hot. The use of carbon tetrachloride has also been suggested (*see* Vol. I., p. 470), since it is not inflammable like the other two solvents and, further, allows of the extraction of the oil from moist substances.

The extraction may be carried out by direct exhaustion or by systematic exhaustion. In the former case, the substance is treated with pure solvent, so that large quantities of dilute solutions which must be concentrated are obtained ; in the other process, a number of apparatus are arranged in a series so that the solvent passes from one to the other and leaves the last completely saturated, while the first apparatus, as it becomes exhausted, is charged with fresh material and placed last in the series (*see* exhaustion of beet in the diffusers, under the heading Sugar, *later*). From the saturated solution of the oil, the solvent

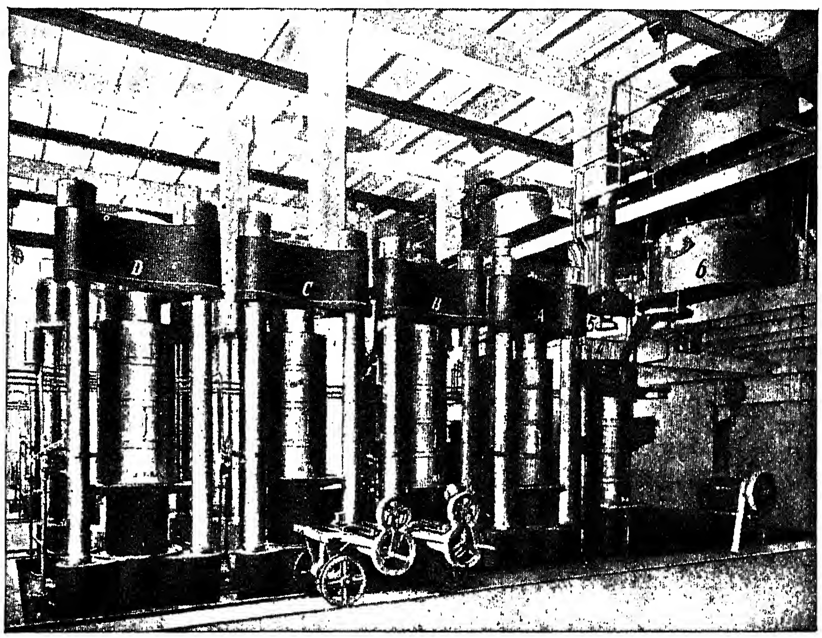

FIG. 278.

is distilled by means of direct or indirect steam and is thus completely recovered, while the crude fat remaining is refined.

There are various forms of apparatus corresponding with the first method of extraction, such as the *Merz universal extractor*, that of Pallenberg, and the Wegelin and Hübner (Fig. 280) form, which is fairly widely used. In the last of these the fatty material is placed in the vessel, A, into which solvent is introduced from D by means of the tube, $r\ q$. The solvent saturated with fat is discharged into the still, C, where, by means of indirect steam passing through the coil, y, the solvent is distilled, its vapour ascending the tube, i, and condensing in B, and the liquid collecting in D. The fat remaining in C can then be drawn off through the tap, x, but if it retains solvent tenaciously, it is first heated by a current of direct steam, solvent and water then condensing together in the condenser, B ; owing to their mutual insolubility, these two liquids can be separated by means of a suitable Florentine receiver [1] situated at w between B and D, the water being thrown out. If the solvent

[1] The Florentine Receiver consists (Fig. 281) of an iron cylinder, D^1, joined at the bottom to the tube, C, and provided with a lateral tube, D, slightly higher than the top of the tube W_1 ($h = 2$ to 4 cm., according to the difference in density between the two liquids to be separated, *e.g.* water and benzine). The tube, B, carries the condensed mixture of water and solvent to the bottom of the separator, the benzine rising to the top and being gradually discharged through

saturated with fat, instead of being drawn off by the tube, *u*, is caused to rise to the top to the tube, *l*, whence it falls into the tube, *v*, the extraction is effected with continuous circulation of the solvent until the substance is exhausted. To expel and recover the solvent

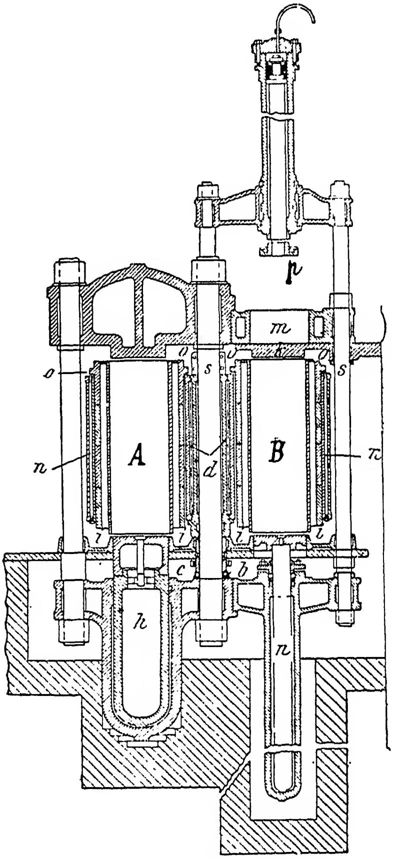

FIG. 279.

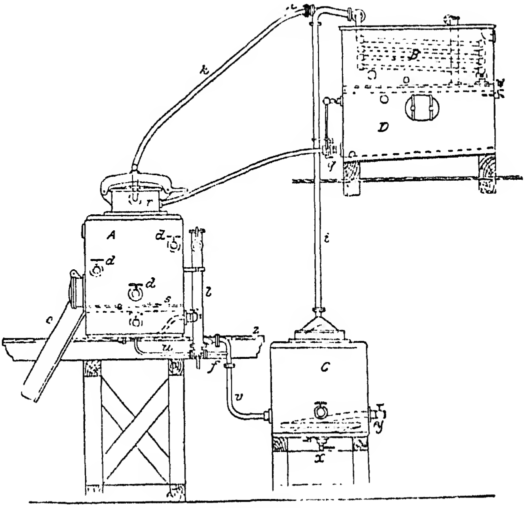

FIG. 280.

retained by the substance remaining in *A*, a current of direct steam is passed into the latter; this carries off the vaporised solvent along the tube, *k*, through the valve, *n*, to the cooling coil, *B*, the condensed water and oil being passed through the separator, *w*, before the latter liquid is collected in *D*.

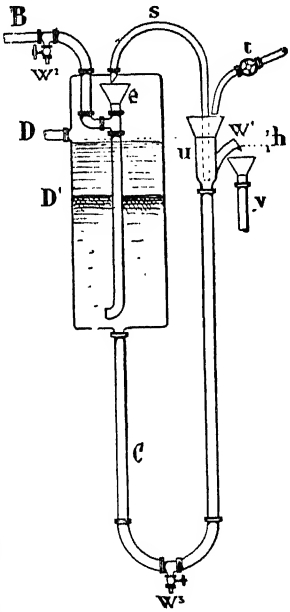

FIG. 281.

By means of the Merz extractor, slightly modified by Fisher (Eng. Pat. 123,645), extraction may be effected in either an upward or a downward direction and also in the hot; the extractor and still, shown in front and side views in Figs. 282 and 283, form a single apparatus, the vapour of the solvent heating the mass to be extracted before it reaches the condenser. The material is introduced at *A* into the cylinder, *B*, having a closed base, *C*, on which are a series of closed coils, *D*, for indirect heating, and the perforated coil, *E*, for the introduction of direct steam, which

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D to the tank (*D*, Fig. 280), while the water is discharged through W_1. At the commencement of the operation water is introduced through the tap, *t*, into *U* until it flows out at W_1; during the distillation a trickle of water enters at *t*. If at any instant irregular distillation causes a sudden excess or deficit of pressure in the separator, either the excess of gas may escape momentarily from *s*, forcing a column of water into *u*, or suction at *s* is absorbed by a small quantity of water falling into the funnel, *e*, which leads it to the bottom of the separator without mixing the benzine and water layers. When a solvent heavier than water, such as carbon disulphide, chloroform, etc., is used, the tube, W_1, is connected with the solvent tank, the water discharging from the tube, *D*. When the extraction is complete and all the solvent has been expelled from the fat and from the residual cake, only water vapour condenses, as may be seen by collecting a sample of the liquid from the tap, W_2.

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serves for expelling the solvent from the extracted mass. Steam enters the coil, F, above which is a double perforated plate supporting the mass to be extracted; at the level of this plate is a rectangular door, G, for the discharge of the exhausted material.

The solvent arriving from the tank through the pipe, H, may be directed to the top or bottom of the mass by the 3-way cock, 2. At the top it enters at K, escapes through the holes of the annular tube, J, is heated by falling over the double steam coil, I, and is distributed over the mass to be discharged through l into the still, below CEF. In order to extract from the bottom upwards, the solvent is passed in at M and overflows the upper perforated plate, N, to collect in the channel, O, and thus pass through P and the inspection glass, Q, into the still beneath.

The still is furnished with a heating coil which can be dismounted and withdrawn, for cleaning or repair, through the manhole, R. Direct steam may be introduced, by the coil, S, to eliminate the last traces of solvent from the oil. The hot solvent vapour surrounds the extractor, keeping the mass to be extracted hot, and escapes at the top of the apparatus through the cast-iron pipe, T, to the cooling and condensing coils. The residual oil is discharged from the still through the valve, 3, at the bottom. The condenser is separated from the solvent tank by a plate, U, and consists of three coils round which the cooling water flows. The condensed solvent passes, together with the steam, into the automatic separator, V (*see* Fig. 282). The steam for the extraction should be at 4 to 5 atmos. pressure and should be dry, and if possible, slightly superheated.

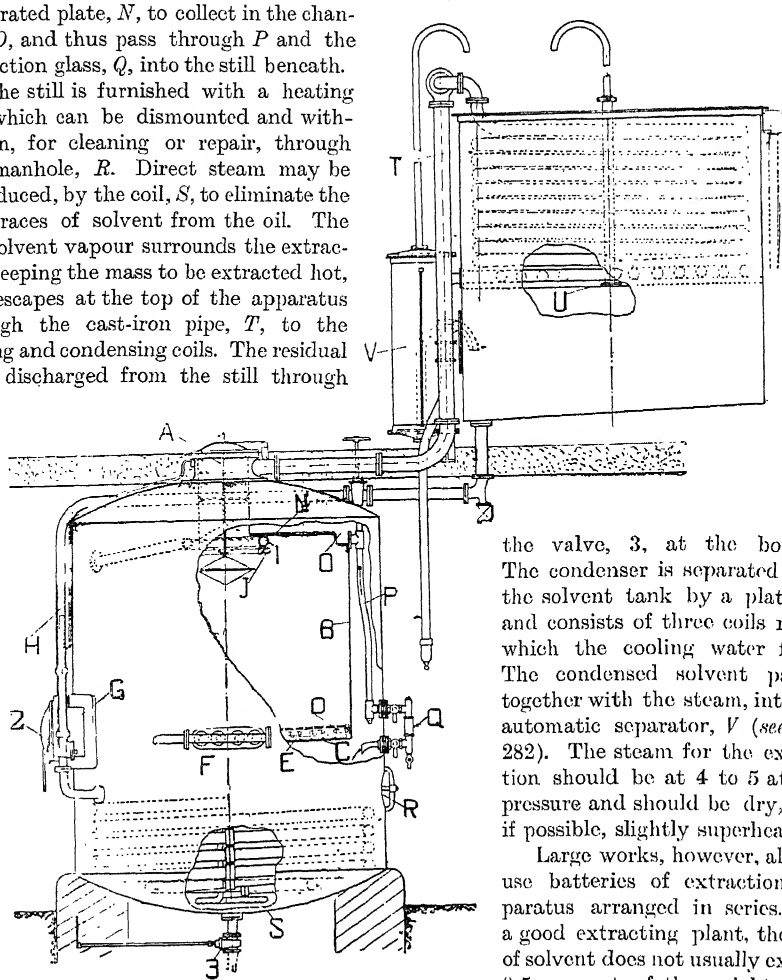

Fig. 282.

Large works, however, always use batteries of extraction apparatus arranged in series. In a good extracting plant, the loss of solvent does not usually exceed 0·5 per cent. of the weight of oil extracted and is always less than 1 per cent.[1]

REFINING of oils, to separate as far as possible the tannins, proteins, and colouring-matters extracted from the oily seeds and fruits, is generally effected by means of dehydrating or oxidising agents (the latter attack the colouring-matters more especially).

In order that sulphuric acid may not act on the glycerides (forming ethers) and heat and partially carbonise the oil, it must be used at a concentration of about 60° Bé. and in small quantity (1 to 2 per cent.) with oil heated to 50° to 60°, or with the cold oil; under

[1] The solvents most commonly used for extracting oils for industrial—not food—purposes are benzine, carbon disulphide, benzene, ether, etc., which are insoluble in water, but are highly inflammable and give explosive mixtures with air. The use of such solvents caused 206 accidents, 60 persons being killed and 187 injured, in Germany in 1911. For this reason increasing use is being made of non-inflammable solvents such as carbon tetrachloride and other chloro-derivatives of hydrocarbons (*see* p. 122).

these conditions the few impurities are first carbonised and the oil becomes coloured, but after filtration it is obtained paler, purer, and clear.

Zinc chloride often gives almost the same results as sulphuric acid, and is added in concentrated solution (sp. gr. 1·85) and in amounts up to 1·5 per cent. of the oil; the black flocculent matter formed separates on standing or filtration.

In some cases it is sufficient to leave the oil in large closed tanks of tinned iron with conical bases fitted with taps so that the impurities which gradually settle may be removed. Fragments of coal, peat, willow, etc., may be added, these carrying down the impurities as they settle. In order to avoid prolonged contact of the oil with the air, pressure filters (described in the section on Sugar) are preferred; either the oil is placed at a higher altitude than the filter, or the pressure is applied by means of pumps, it being possible in this way to filter 1000 to 2000 kilos of oil in 24 hours. To purify with sulphuric acid (*see later*, Twitchell process), the latter is poured in a thin stream into the oil contained in a lead-lined vat and kept well stirred. After seven to eight hours, by which time small black clots of carbonised impurities have deposited, the oil is decanted into a second vat, washed two or three times with water at 40° to 60° (in some cases a small quantity of sodium carbonate is added to the second water), being stirred meanwhile or emulsified by air from a Körting injector; after being left to stand, it is either decanted or filtered.

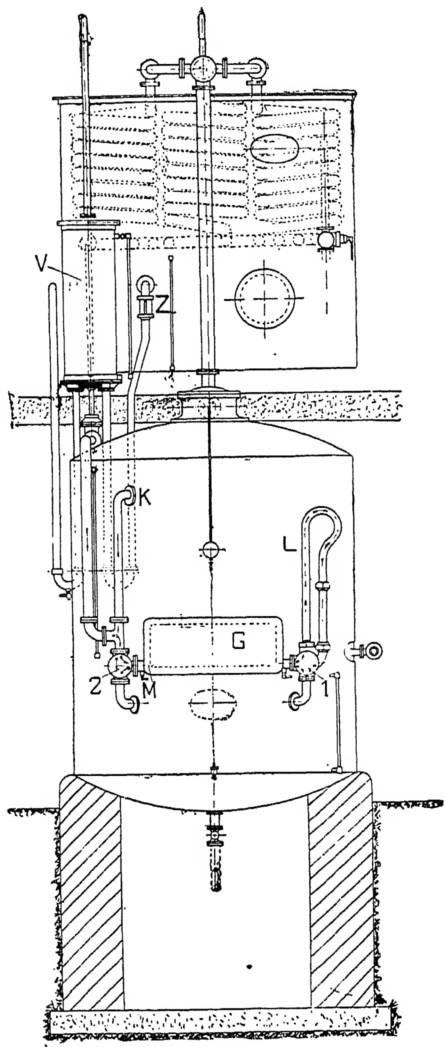

FIG. 283.

The water is sometimes intimately mixed with the oil to be washed by means of the so-called *emulsor-centrifuge* (Fig. 284), consisting of two superposed metal plates with the concave parts inside and mounted on a hollow axle rotatable at 8000 to 10,000 revs. per minute, while through a central aperture commanded by two taps—exactly adjustable —the oil and water are introduced in the desired proportions. The distance between the two plates can be altered so as to give a slit between their edges from 0·02 to 2 mm. in width, the more or less completely emulsified mass being forced out through the slit by the plates themselves. If the oil does not separate from the water on standing, the emulsion may be destroyed by adding powdered and calcined sodium sulphate or carbonate (which act as dehydrating agents) or by agitating the emulsion with animal black or magnesium silicate (which separates the components), but the best results are obtained with *centrifugal separators*, like that used for milk (*see* p. 476), the water and impurities being forced to the periphery, where they adhere, while the oil is discharged by the central tube. The acid also may be mixed in the same way, and continuous working may be attained by means of a battery of emulsors and another of centrifugal separators; the latter serve well to purify the dregs of the oil and, in general, colloidal and soapy products of oils. When the emulsified or colloidal condition is due to the presence of gum or wax, it is preferable to initiate freezing of the glycerides, this breaking down the emulsion so that it can be filtered. When *stable emulsions* of oil and water are required, as is sometimes the case, they can be obtained by pouring the oil, mixed with salified stearo-anilide, into a boiling mixture of water and

aminostearic acid; when mixed, the dense emulsion is stable, even in the cold (Kösters, 1907).

To *deodorise* oils, they are passed through bone-black or, sometimes, elm-bark. The passage of superheated steam through the oil heated to about 200° gives better results. In some cases, and more especially when very rancid, oils are purified by *deacidifying* them with a concentrated solution (8° to 10° Bé. for cottonseed oil and 36° to 38° Bé. for olive oil) of caustic soda in amount slightly exceeding that calculated from the acid number; this treatment, however, readily leads to the formation of persistent emulsions and to loss of glycerides and also of fatty acids. These emulsions, which are due to the presence of soaps, are broken down in the manner already described, first being heated to 50° to 60°. Emulsification is sometimes avoided by adding sufficient lime or ammonia to neutralise the free acidity and then completing the refining by the passage of steam. If the acidity exceeds 30 per cent., the losses would be so high that deacidification is not advisable; such oils (*e.g.*, highly acid olive oil after refining with sulphuric acid) cannot be used as lubricants or for softening wool, but are used solely for soap, unless indeed the fatty acids are transformed into glycerides by treatment with glycerine as described on p. 461.

Bleaching with hydrogen peroxide, dichromate or permanganate is carried out as with tallow (*see* p. 470), but if the oil is first deacidified, 1 kilo (instead of 15 kilos) of dichromate per ton is sufficient. If it is required to eliminate every trace of soap, the oil is heated with a boiling solution of 5 per cent. sulphuric acid. Vegetable oils are frequently decolorised nowadays with fuller's earth (*see* Vol. I., p. 738),[1] and good results are obtained also by heating with alkaline solutions of sodium hydrosulphite.

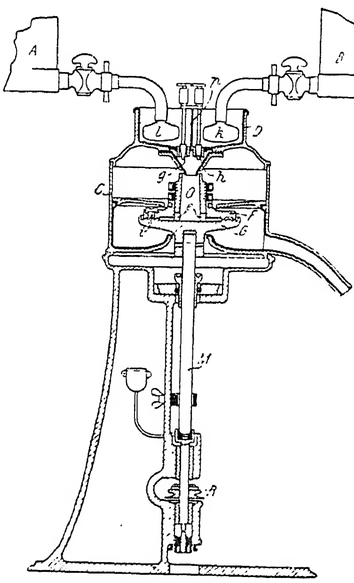

FIG. 284.

OLIVE OIL is obtained by pressing the fresh olives of *Olea europaea* in the period from October to December (in Morocco, in August and September). The olive grows in abundance in Central and Southern Italy, on the shores of Lake Garda, on the Genoese Riviera, and in Southern France, Spain, Portugal, Dalmatia, Istria, Greece, Morocco, California, and Southern India.

The composition of the fruit is given in the Table on p. 482.

It is not advisable to extract the oil from stored or fermented olives, these giving the so-called *huile tournante*, which is rich in fatty acids and yields a persistent emulsion when shaken with soda solution, and a *Turkey-red oil*—similar to the sulphoricinate (*see* p. 390)—when treated with concentrated sulphuric acid.

If the olives cannot be worked at once, fermentation is prevented by storing them in a cold, dry, and well-ventilated place. The fermentation (according to Tolomei) is due to an enzyme (*olease*) occurring with the oil, which, in the presence of air and light, it decolorises; if the olease is removed by washing the oil with water, the oil is not decolorised under the influence of light.

The extraction of olive oil is not always effected by rational processes and plant, but usually the olives are first crushed by means of the ordinary edge-runners (*see* Fig. 185, p. 269).

[1] Fuller's earth has been long used in Northern Africa for clarifying olive oil; in Chicago it was thus employed as early as 1878, but its use was considerably extended subsequently to 1890. It consists of aluminium and magnesium hydrosilicates, and is found in granular or powdery deposits in Florida and also at Fraustadt, in Silesia. The decolorising action of this earth depends on its state of hydration, the maximum effect being obtained if it is first lightly roasted (at about 200°), while if the roasting is carried too far so that all the water of hydration is lost, the decolorising power is entirely destroyed. The oil is shaken with 1 to 3 per cent. of the earth, and the mass heated for a short time at a temperature (60° to 100°) varying with the nature of the oil and then passed to the filter-press, the first turbid portions of the filtrate being refiltered.

The pulp is next placed in suitable bags of tenacious vegetable fibre or wool surrounded by horsehair and then pressed, the type of press employed varying widely with the locality. The ring hydraulic press (*see* Fig. 275, p. 485) and other forms, still further improved, give excellent results. In some cases a moderate pressure is first employed, the result being oil of superfine quality (*virgin oil*). The residues are steeped in hot water and subjected to increased pressure. Repetition of this procedure, employing a still higher pressure, gives an industrial oil. The cake from the second pressing may, however, be agitated in a vat through which water flows; part of the remaining oil is thus removed, this being collected in a second vat, where it undergoes protracted washing with water, yielding so-called *washed oil*.

The Kuess-Funaro process (1902), which results in an improved yield and a readier extraction, consists in emulsifying each time with feebly alkaline aqueous solution.[1]

The residual cakes (known in Italy as *sanse*), after being dried, still contain [illegible] to 11 per cent. of oil, which is nowadays extracted in large works by means of carbon disulphide, which gives the very green, so-called *sulphocarbon oil*, almost all of this being used in the manufacture of green soap for the textile industries.[2] This soap is sometimes called *Marseilles soap*, and is used especially for the treatment of raw silk; in France, however, and to some extent in Italy, this name is given to high grade white soap, mostly prepared from copra and arachis oils.

Pure olive oil is yellowish or, in some cases, almost colourless or slightly green. The finer qualities taste but little; freshly pressed Puglia oil has a rather bitter and unpleasant taste (due to camphene, eugenol, and other substances investigated by Canzoneri, which it gradually loses.

The *composition* of olive oil varies with the district of origin and with the conditions of extraction, the solid glycerides fluctuating from 10 to 28 per cent. (more especially palmitin). The liquid glycerides, which occur to the extent of 70 to 90 per cent., were formerly thought to consist of triolein alone, but the presence of linoleic acid (as much as 6 per cent., this explaining the high iodine number of the oil) has now been proved, and there appears also to be about 1·5 per cent. of a mixed glyceride and 0·2 to 1·5 per cent.

[1] A new process of extracting olive oil proposed by Acapulco (1910–1911), and tested with favourable results in the experimental oil plant of the Portici Higher Agricultural School, is based on the different surface tensions of the two liquids (oil and water) which are present in the pulp of the olive and have to be separated, and hence on their different capillary behaviour towards the vegetable tissues constituting the pulp. The surface tension of the oil is about one half that of the water, so that separation of the two liquids is easily attained by even slight diminution of the pressure below that of the atmosphere. The separation is also facilitated by rise of temperature and by the fact that the water present has a capillary constant higher than that of the oil, so that it remains more strongly adherent to the vegetable tissues. The essential part of the machinery of this process—after the stones have been separated from the pulp—consists of the so-called filtering extractors, formed of superposed metallic cylinders, inside which is a metal filtering cloth, an annular space communicating with the vacuum pump being left between the walls and the cloth. A stirrer fitted with vanes continually moves the mass of pulp contained in the extractor and spreads it in thin layers on the filtering cloth so that the liquid portion is separated from the pulp. By steam heating the extraction can be carried out at any temperature, but even in the cold the exhaustion of the pulp is more complete than that obtained by the older systems, while in the hot it surpasses that reached by pressure the [illegible] in the most powerful hydraulic presses. It is said that the Acapulco process is more economical than those previously used and that it lends itself to the production on a large scale of pure, slightly coloured oils of constant type, but, as yet, this process has not been subjected to decisive commercial tests.

[2] To distinguish *sulphocarbon oil*, which has a lower iodine number (77 to 80), from that obtained by pressure, Halphen's test may be employed. To 50 c.c. of the oil heated to 100° is added 12 c.c. of alcoholic caustic potash diluted with an equal volume of water, the mixture being heated for 10 minutes at 110° and cooled to 100°; 200 c.c. of hot water is then added and the liquid, after cooling, shaken with 200 c.c. of saturated sodium sulphate solution; 20 c.c. of 30 per cent. copper sulphate is then added, and the liquid filtered. If the filtrate is not green a little more of the copper sulphate solution is added and the liquid filtered again if necessary. 5 c.c. of silver nitrate solution (containing 1 vol. of 1 per cent. aqueous silver nitrate solution and 5 vols. of glacial acetic acid) is then added to the liquid, which is boiled, allowed to cool, supersaturated with ammonia and filtered, the filter being washed with dilute ammonia. If black silver sulphide remains on the filter, the presence of sulphocarbon oil (or *impure* cruciferous oils—colza, mustard, etc.—which cannot be detected otherwise) is certain. [illegible] (1909) has devised a simple test: 200 grms. of the oil is vigorously shaken with 50 grms. of 90 per cent. alcohol and then distilled on a water-bath, the distillate being collected in a well-cooled flask containing a little alcoholic potash. Even traces of carbon disulphide thus yield potassium xanthate, which gives a yellow coloration or precipitate on addition of alcoholic cupric acetate solution.

of volatile acids, besides 0·7 to 1·6 per cent. of non-saponifiable substances (phytosterol and, according to Sani, an oil not yet defined). It contains a variable quantity of free fatty acids, and when impure readily becomes rancid. If the acid number exceeds 16 (*i.e.*, 8·1 per cent. of acids calculated as oleic acid), it cannot be used as machine oil, as it attacks metals.

Pure olive oil is used as a comestible and the very pure and more liquid qualities for oiling clocks, while the other qualities are employed in large quantities in the manufacture of soap, lubricants, burning oil, and Turkey-red oil.

The purity of the oil is controlled by various tests referring to the constants given in the Table on p. 466, and by certain special tests. Olive oils of certain origins give abnormal constants, *e.g.*, Algerian and Moroccan oils have an iodine number of 96 and are reddened by nitric acid; pure Tunisian olive oil gives the reaction for sesamé oil (Villavecchia and Fabris' test) but not the Belliez reaction (test for sesamé oil with a saturated solution of resorcinol in benzene and nitric acid); the extraneous substances of Tunisian oil which give the Villavecchia and Fabris test can be removed by shaking the oil with hot water. Detection of added *sesamé oil* is effected by Tortelli and Ruggeri's modification of Baudouin's test on the fatty acids (*see* p. 472), or more rapidly on the oil itself by means of Villavecchia and Fabris' test, taking care to dilute 5 c.c. of the resulting red acid liquid with four times its volume of distilled water and to shake the mixture in a cylinder, and observing the lapse of time required for the disappearance of the red coloration. With *any* pure olive oil, if there is a coloration, this disappears within five minutes or, in exceptional cases, in eight minutes, whilst if sesamé oil (even only 3 per cent.) is present the colour will persist for 30 minutes (Zega and Todorovic, 1909). The presence of *cottonseed oil* is indicated by the Halphen reaction (*see* p. 470) or by Tortelli and Ruggeri's modification of Becchi's reaction, which is carried out on the liquid fatty acids in the following manner: 20 c.c. of the suspected oil is hydrolysed with alcoholic potash in the ordinary way (*see* p. 468), the aqueous solution of the soap being neutralised with acetic acid and precipitated with lead acetate; the lead salt, separated by filtration, is shaken with ether and the filtered ethereal solution decomposed in a separating funnel by dilute hydrochloric acid. The ethereal layer is filtered and the ether evaporated, and to 5 c.c. of the residue (liquid fatty acids) [1] are added 10 c.c. of 90 per cent. alcohol and 1 c.c. of 5 per cent. aqueous silver nitrate solution; if a black precipitate is then formed on heating for some time on a water-bath at 60° to 70°, the presence of cottonseed oil is proved. In certain special cases the Becchi reaction alone is insufficient to indicate with certainty the presence of cottonseed oil. Traces of *mineral oils* in vegetable oils are detected by the formation of a yellowish red solution on addition of a benzene solution of commercial picric acid (F. Schulz, 1908; *see* Note, p. 468). To detect *fish oli* in vegetable oil, 100 drops of the latter are treated with a mixture of 3 c.c. of chloroform and 3 c.c. of acetic acid, sufficient bromine being then added to produce a persistent brown coloration; after 10 minutes' rest the vessel is introduced into boiling water, when the liquid will remain liquid if the vegetable oil is pure, whilst insoluble bromo-compounds will separate if fish oil is present. With boiled oil, the metals are first eliminated. Where the oil has been coloured yellow with *auramine*, this is detected by boiling 1 c.c. of the oil with 20 c.c. of 8 per cent. alcoholic potash and a little zinc dust in a reflux apparatus, 20 c.c. of pure benzene and 50 c.c. of water being added after cooling; the benzene solution is evaporated and the residue taken up in glacial acetic acid, a blue coloration, becoming darker on heating, being formed if auramine is present. *Sanse oil* or sulphocarbon oil, extracted from the cake or *marc* by means of carbon disulphide, has a dark green colour, and the corresponding fatty acids have a rather low iodine number (as low as 75) and a somewhat higher melting-point than usual.

The presence of *arachis oil* in olive oil is shown by the Tortelli and Ruggeri test, which has been modified by Fachini and Dorta (1910) as follows: 20 grms. of the oil is saponified with alcoholic potash, the alcohol being then expelled, the soap dissolved in water, the fatty acids liberated by hot dilute sulphuric acid, and the clear fused acids collected on a moist filter; they are then washed with hot water and dissolved in 150 c.c. of pure, tepid acetone, water being subsequently added, drop by drop, until a turbidity is formed; the liquid is

[1] The *liquid fatty acids* can be separated, to a considerable extent if not quantitatively, from the solid ones by dissolving the mixtures in light petroleum or, better, in acetone and crystallising out almost all the solid fatty acids by cooling to $-20°$ (Fachini and Dorta, 1910). According to Twitchell (U.S. Pat. 918,612, 1909) the liquid fatty acids are separated from the solid ones by fusion with 1 per cent. of aliphatic sulpho-acids, which render the liquid acids soluble even in water.

finally rendered clear by the addition of a few drops of acetone at 40° to 45° and then left to crystallise. In presence of arachis oil, characteristic shining crystals separate at 15°; after an hour these are collected on a filter, washed with 10 c.c. of dilute acetone (32 vols. water + 68 vols. acetone) and examined for arachic and lignoceric acids by the Tortelli and Ruggeri test: one-half is dissolved in 100 c.c. of 70 per cent. alcohol, warmed slightly and allowed to cool, separation of crystals indicating arachidic acid (m.-pt. 75° to 76°) with certainty.

STATISTICS.—The cultivation of the olive is widespread in Italy and Spain, the output of oil (tons) being as follows:

	1907	1910	1914	1916
Italy	260,540	124,610	160,560	206,200
Spain	306,415	108,510	207,765	207,115

Owing to the high price of coal during the European War, the old olive trees were largely burnt as fuel. Portugal produces annually about 25,000 tons of olive oil, Algeria about 32,000 tons, and Tunis about 36,000 tons. The output and price vary with the season and with the demand. In some years the producers sell at £4 and in others at about £2 10*s.* per hectol., but during the European War far higher prices were obtained.

FIG. 285.—*Ricinus communis*: Shoots with flowers, male below and female above.

1, stamens; 2, anthers, magnified; 3, ovary with three stigmata; 4, fruit, half size; 5–8, sections of fruit; 9–12, seeds and sections thereof.

CASTOR OIL is extracted from the seeds of *Ricinus communis* (Fig. 285), a plant cultivated in India, Indo-China, Java, Italy, Mexico, California, Egypt, Algeria, Tunis, Paraguay, Argentine, United States, Spain, and Greece. The oval seeds are 10 to 15 mm. long, about 6 mm. broad, and rather flat, and are covered with a brownish or marbled, shining, brittle skin; when peeled they contain 45 to 55 per cent. of oil. The seeds contain about 19 per cent. of nitrogenous substances and an enzyme capable of hydrolysing the fats into free fatty acids and glycerol (*see* Soap). The husks of the seeds contain poisonous substances (*ricin, ricinin*), which do not pass into the oil, but the pressed cake cannot be used as cattle food, and is employed as fertiliser, as it contains about 4 per cent. of assimilable organic nitrogen, 2 per cent. of P_2O_5 and 1·12 per cent. of K_2O.

The oil was at one time extracted by pressing the ground seeds twice in the dry state and then pressing the residue after steeping in hot water. Nowadays, however, three consecutive pressings of the hot crushed seeds with increasing pressures are employed, modern hydraulic presses being used. This procedure yields first a fairly pure pale oil, then one less pure, and finally a more highly coloured oil for secondary industrial purposes. One hundred kilos of the seeds yield 9 kilos of husks, 43 of residual cake (with 8 per cent. of oil), 20 to 25 of oil of the first, 6 to 8 of the second, and 4 to 6 of the third pressing. The oil is purified by heating with an equal volume of boiling water, which precipitates many protein and gummy substances; it is decolorised by means of bone-black or by the ordinary processes given for tallow. The medicinal oil is obtained by a first cold pressing, and is then filtered in a vacuum to prevent rancidity.

The refined oil is almost colourless or faintly yellow, and has a high specific gravity, considerable viscosity, and a peculiar, unpleasant taste and smell. It forms an excellent purgative, the less pure qualities being used in the manufacture of *sulphoricinate* (*see* p. 390) and of transparent soaps capable of retaining considerable quantities of water. It is used for softening leather and for making pegamoid. Its soap differs from others in not rendering water opalescent.

Its specific gravity mostly lies between 0·961 and 0·964, and it freezes between − 12° and − 18°, and owing to its high viscosity even at high temperatures, its slight solubility in benzine, and the small amount of solid residue left on combustion, it serves as an excellent lubricant for high-speed engines (for aeroplanes, etc.).

Castor oil contains various glycerides but is free from tripalmitin. Triricinolein is solid, and there appear to be glycerides of a *ricinoleic acid* and of a *ricinisoleic acid*, also of a hydroxystearic acid (melting at 141° to 143°) and a dihydroxystearic acid (which explains the characteristic high acetyl number of castor oil).

The oil yields, besides ricinoleic acid, more or less highly polymerised compounds with less and less marked acid characters (*e.g.* ricinisoleic acid), these increasing in amount with the age of the oil.

Castor oil is strongly dextro-rotatory (24 to 25 saccharimetric degrees in a 20 mm. tube). Unlike other oils, it is soluble in all proportions in absolute alcohol, glacial acetic acid, or ether; at 15° it dissolves in 2 parts of 90 per cent. alcohol or 4 parts of 84 per cent. alcohol, but is insoluble in light petroleum or vaseline oil (which dissolve all other oils and fats). Hence, if a castor oil is insoluble in light petroleum and gives a clear solution with 5 vols. of 90 per cent. alcohol, it may be regarded as pure. The solubility relations are completely inverted if the oil is heated to 300° and 10 to 12 per cent. of it distilled; there then remains a product termed *floricin*, which solidifies at − 20°, is insoluble in alcohol, dissolves in all proportions in mineral oil, and forms a stable emulsion with 5 parts of water. A similar product is also obtained by heating castor oil to 200° in presence of 1 per cent. of formaldehyde; if heated with zinc chloride solution, it thickens. The potassium salt of the thickened product, with water and formaldehyde, gives a disinfectant solution producing the same effects as lysoform or ozoform.

The constants of castor oil are given in the Table on p. 466.

LINSEED OIL is a drying oil, as it contains much linoleic and linolenic acids (*see* pp. 363 and 364), and when spread out in a thin layer on a sheet of glass slowly forms a solid skin (varnish), this forming more rapidly with the boiled oil.

Linseed oil is extracted from the seeds (containing 35 per cent. of oil) of *Linum usitatissimum*, which are converted into flour by the ordinary edge-runner mills and pressed hot in hydraulic presses.

Linseed is cultivated especially in the Baltic provinces of Russia, and also in Southern Russia, Eastern India, the United States, and the Argentine, and to a less extent in Egypt, Belgium and Italy. Linseed oil extracted by means of solvents contains more unsaturated fatty acids and less volatile acids than the expressed oil.

According to Fahrion (1903 and 1910), the fatty acids separated from linseed oil contain 17·5 per cent. of oleic acid, 30 per cent. of linolic acid, 38 per cent. of linolenic and iso-linolenic acids, 8 per cent. of palmitic and stearic acids, all combined with 4·2 per cent. of glycerine and 0·6 per cent. of non-saponifiable substances.

The purity of the oil is indicated by means of the constants given in the Table on p. 466, especially by the iodine number and the refractive index, which, in the different qualities, varies from 1·484 to 1·488 at 15° (or from 81 to 85 Zeiss at 25° or 87 to 91 Zeiss at 15°), whilst cottonseed oil gives no more than 1·477 and maize oil no more than 1·4765 at 15°.

A good proportion of the oil is used in the form of *boiled linseed oil* (*see* Note on next page), since on boiling it acquires drying properties especially necessary to the varnishes prepared with the oil.

The *drying power* may be determined by Livache's method. On a watch-glass is spread 1 grm. of lead-powder (obtained by immersing a strip of zinc in the solution of a lead salt and washing the precipitate with water, alcohol and ether, and drying), on which 0·6 to 0·7 grm. of oil is allowed to fall slowly in drops, the whole being then weighed exactly and left at a moderate temperature in a well-lighted situation. After 18 hours the weight begins to increase, the maximum increase (12 to 15 per cent.) being obtained within two or at most three days (it then diminishes slightly). Other drying oils give the following increases: *walnut oil*, 7·9 per cent.; *poppyseed oil*, 6·8 per cent.; *cottonseed oil*, 5·9 per cent.

cod-liver oil, 7·4 per cent.; the remaining oils increase in weight only after the fourth or fifth day to a maximum of 2·9 per cent. after seven days. The *drying properties* are determined best and most rapidly by spreading a given weight of the boiled linseed oil on a definite area of glass (1 mgrm. per sq. cm.) and leaving the latter in a horizontal position until the oil is no longer adhesive when pressed lightly with the finger (the temperature should always be noted). The drying power of an oil may be determined also from the ozone number (Molinari and Scansetti, 1910).

In a 20mm. tube, pure linseed oil gives a rotation of $-0·3°$ in the Laurent saccharimeter at 15°, whilst other resin oils and sesamé oil are dextro-rotatory.

Linseed oil is used mostly in the manufacture of *lacs* and *varnishes*,[1] mastics and *lino-*

[1] **Oil Varnishes and Lacs** are liquids which, when spread out in a thin layer on an object, leave on drying a solid, shining skin insoluble in ether and water and almost impermeable. Varnishes and lacs have linseed oil as a basis, and are often mixed with mineral or organic colouring-matters. Oil varnishes are formed from linseed oil rendered drying by dissolving small quantities of certain minerals in the hot. Oil lacs are obtained by adding to the almost boiling oil varnish (free from gummy matter) fused copal or other resin, and diluting with oil of turpentine at the moment of using: all these new components contribute to increase the fixation of oxygen.

Copal is a resin derived from various species of more or less fossilised plants. The harder copals melt at temperatures up to 300 °and the softer ones at 100°. They have specific gravities lying between 1·035 and 1·07, and they dissolve partially in ether, alcohol, benzene, acetone or chloroform, and almost completely, but slowly, in a mixture of alcohol and ether; they are insoluble in petroleum ether, fatty oils and oil of turpentine, but soluble in rubberseed oil or copal oil (from the distillation of copal). To render them soluble in linseed and other oils and in oil of turpentine, they are heated for 6 to 10 hours at 300° to 320°, best in presence of either stearic acid or the fatty acids of linseed or castor oil. Copal consists of resin acids (*trachylolic* and *isotrachylolic acids*), resens (copal resens), a bitter substance and an essential oil. The acid number varies from 80 to 150, the iodine number from 58 to 70, and the saponification number from 100 to 165. Before the European War copal was sold at 32*s.* to 100*s.* per cwt.

Crude linseed oil requires four to five days to dry in a thin layer, but the fixing of oxygen, that is, the drying, may be markedly accelerated by the presence of small quantities of dissolved metals which act as catalysts.

At one time oil varnish (boiled linseed oil) was prepared by heating the oil to 220° to 300° for two to three hours in presence of minium, litharge, or manganese dioxide (*dryers*). This procedure yielded dark varnishes (*boiled varnishes*), and was accompanied by danger from fire, the heating being carried out in open iron vessels furnished with stirrers and heated directly over the fire. Nowadays the dryer (0·1 to 0·25 per cent. Mn or 0·5 per cent. Pb + 0·1 per cent. Mn is sufficient) is dissolved by heating at a far lower temperature (100° to 120° and best in a vacuum) for four or five hours (by indirect steam at 135° to 150°), it being added (when the oil ceases frothing) as manganese borate or, better, manganese linoleate or resinate, and the mass stirred with compressed air; in this way, the so-called *cold varnishes* are obtained. These are paler varnishes which dry in 6 to 8 hours, whilst the others require as long as 24 hours. It has been proposed to decolorise boiled linseed oil with ultra-violet rays. The *drying* is far more rapid in the hot than in the cold. Prolonged boiling of linseed oil without dryers increases not so much the drying properties as the consistency, certain components of the oil being polymerised and linoxyn formed, and the iodine number consequently diminished (*e.g.*, from 154 to 27); these oils, thickened at 295° to 340°, bear the names *Dicköl, Standöl,* and *lithographers' varnish.* The action of oxygen during the drying of varnishes seems to lead to the decomposition of the glycerides of the saturated acids and of oleic acid with subsequent complete oxidation of the glycerine and acids, the glyceride of hydroxylinolic acid (*hydroxylinolein*), insoluble in ether, being also formed as well as anhydrides and polymerised substances. If 2 to 3 per cent. of pyridine, quinoline or other organic base is added to a linseed oil varnish, cracking will not occur, even after years (Ger. Pat. 239,289, 1908).

In the manufacture of *lacs*, a difficult and important operation is the fusion of the copal previously prepared in lumps—in cylindrical or slightly conical, enamelled iron or aluminium vessels; these are protected at the bottom by an iron or copper casing when heated by direct fire heat and are provided with a cover and chimney to carry off the noxious vapours, which are carefully condensed or burnt. The temperature is closely watched by means of a thermometer immersed in the fused copal (300° to 360°). It is nowadays regarded as preferable to heat with hot water under pressure (up to 300°) circulating in coils situate in the lower part of the boiler. Complete, uniform fusion occupies 3 to 4 hours (with a loss in weight of 15 to 30 per cent.), the linseed oil containing the dryer and heated to about 100° being then mixed in; if any turbidity appears, the mass is heated to 300°. It is then allowed to cool to 150° to 200°, the addition of the oil of turpentine—which dissolves the lac—and, if necessary, of the dryer, being then begun. The diluted lac is filtered under pressure and discharged into smaller vessels, in which it is allowed to cool completely. The addition of calcium salts of colophony renders the lac harder but more brittle.

The copal is sometimes replaced by colophony and other resins, which are, however, readily saponifiable; a mixture of Japanese wood oil with resin and a little lime gives a good lac. Lacs are improved by prolonged storage (at least a year). Linseed oil for making lacs should be free

leum. The last, first prepared by Walton in 1860 and improved by Parnacott and Taylor, is obtained by oxidising (blowing) hot linseed oil, after addition of the dryer (*see* Note), for 18 to 20 hours with hot air until it thickens to linoxyn; about 30 per cent. of colophony is then added, the whole being converted into a paste with cork-dust at a temperature exceeding 100°. The mass swells and is compressed hot (140°) on a strong textile previously varnished to protect it from moisture, the whole being repeatedly pressed between hot rollers. It is finally dried for some weeks in suitable chambers at 30° to 35°, where it loses its smell and acquires elasticity and weight. It is coloured in the pasty condition with mineral colouring-matters. According to Bitter (1911) linoleum exerts a marked germicidal action.

Lincrusta also is made from linoxyn, a stream of air being passed through linseed oil at 100° for some days until a dense mass is formed. This is mixed with white chalk and other pigments and cement, the mixture being spread and pressed on to strips of paper by means of hot rolls which impress designs on to the surface.

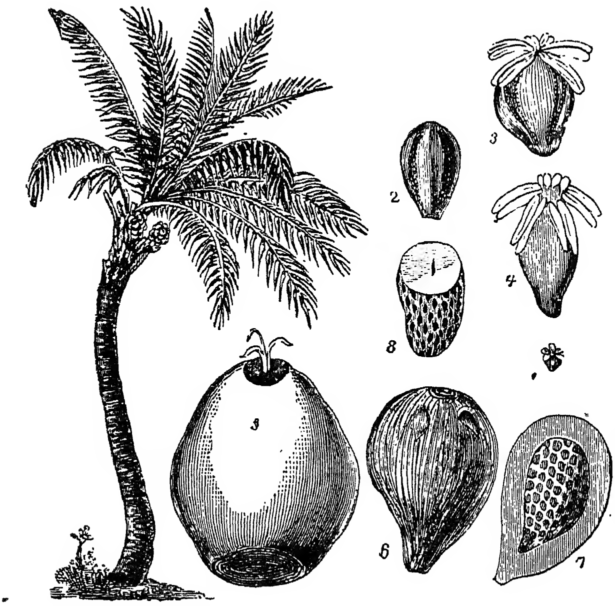

FIG. 286.—Oil palm (*Elais guineensis*).

1, male flowers; 2 and 3, male flowers, magnified; 4, stamens; 5, fruit with three stigmata; 6, nut with three apertures at the top; 7, section of the nut with the seed inside; 8, transverse section of the seed.

Linseed oil is used also for making soft, transparent soaps (*see* later).

The mean annual production of linseed throughout the world in 1907–1916 amounted to about 2,750,000 tons.

WALNUT OIL.—This is a drying oil like linseed oil. The fresh nuts are freed from the outer green husk and left to dry for some weeks, after which they are stored in heaps for 3 to 4 months; this treatment increases the yield of oil and leads to the disappearance of the milky juice of the nuts, which would be difficult to separate from the oil. After removal of the shell, the dried nuts give 25 to 30 per cent. of fruit yielding 30 to 35 per cent. of pale yellow, virgin oil in a first pressing in bags in the cold, and a further 15 to 20 per cent. of greenish oil when the residual cake is broken, treated with hot water and pressed hot. The fresh virgin oil is sometimes used as a comestible, but it quickly turns rancid and has a pronounced flavour; it is used more commonly for lighting and as a drying oil for varnishes and for artists' use.

It contains glycerides of oleic, linoleic, linolenic, lauric and myristic acids and has the specific gravity 0·925, iodine number 142 to 152, saponification number 186 to 197, Tortelli thermo-oleometer reading 104°, Zeiss butyro-refractometer reading 64 to 68 at 40°, melting-point of the fatty acids 16° to 20°.

PALM OIL is extracted from the fruit of certain varieties of palm (*Elais guineensis* and *Elais melanococca*, which grow in Western and Central Africa and in America, and *Astrocaryum acuale* and *Astrocaryum vulgare*, growing in Guiana). The orange-brown fruit, of the size of walnuts, hangs in bunches; each bunch weighs 10 to 20 kilos and contains 1000 to 2000 fruits, and each plant yields, on the average, four bunches per annum.

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from gummy matters, which may be removed by filtration through Florida earth (*see* p. 490 and Vol. I., p. 738). The softer lacs contain more than 50 per cent. and the harder ones less than 50 per cent. of linseed oil.

The pulp constitutes, according to the variety, 25 to 75 per cent. of the fruit, which contains a nut, and this a white seed also yielding an oil (*palm-nut* or *palm-kernel oil*: *see* Fig. 286).

The extraction of the oil in the districts where the palm is grown is carried out in an irrational manner, the fruit being sometimes heaped up until it putrefies and the oil then pressed out. In other cases the fruit is stored and compressed in excavations in clay soil, being left to putrefy until the oil separates at the surface. In other places the fruit is fermented for a month and then heated with water, so that the pulp becomes detached from the stone and can then be heated and pressed again with water until the fused oil comes to the top and can be decanted off. In these ways more than one-half of the oil is lost, and machinery is now being introduced for detaching and disintegrating the pulp and for the rational pressing of the latter.

When freshly expressed, the oil has a buttery consistency, an intense orange-yellow colour and a faint smell of violets; the colour and odour persist in the soap prepared from it. It can be decolorised by heating it when exposed to the air and light, but this is effected best and most rapidly by fusing and heating it until it loses the water remaining from any preliminary heating with water for the removal of impurities; this separates from the fused mass in 24 hours. After this it is introduced into a metal vat or cylinder (Fig. 287) provided with a cover and tube for carrying the gases to the chimney; the fat is heated to 120° to 130° by means of an indirect steam coil, *VP*, and a vigorous and finely divided stream of air passed through the oil from a perforated tube, *R*. In 3 to 4 hours' decolorisation is complete; at the same time the pleasant odour of the fat remains, although it is destroyed if the fat is decolorised by simple heating to 220°.

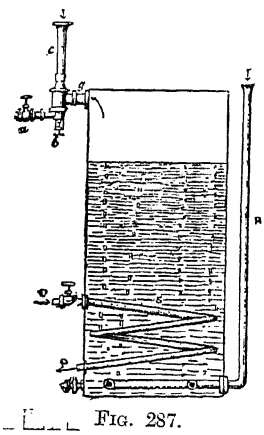

Fig. 287.

Chemical decolorisation is often employed, the oil (1000 kilos), already purified by treatment with water and by fusion, being heated in a boiler to 50°, at which temperature 30 to 50 kilos of commercial hydrochloric acid and 8 to 10 kilos of potassium dichromate dissolved in 18 to 20 litres of boiling water are stirred in. After 15 to 20 minutes, 1 to 2 kilos of sulphuric acid are sometimes added, the stirring being continued until the oil becomes limpid; stirring is then stopped and 70 to 80 kilos of boiling water sprayed on the oil to wash it. After standing overnight, the water is decanted off, the acid separated from below, and the oil washed once or twice by boiling with water.

Even when fresh it contains 12 per cent. of free fatty acids, and as it becomes older it decomposes spontaneously with increasing ease, separation of fatty acids (up to 55 per cent.) and glycerine—which can be extracted with water—taking place. Besides free palmitic acid, the principal components are the glycerides of oleic and palmitic acids, up to 1 per cent. of stearic acid, a little linolic acid, and about 1 per cent. of heptadecylic acid, $C_{17}H_{34}O_2$.

The colouring-matter of palm oil admits of various characteristic colour reactions: with sulphuric acid, a bluish green coloration is obtained, whilst mercurous nitrate colours it first canary-yellow, then pale green, and finally straw-yellow.

Palm oil is used in large quantities in the manufacture of soap and candles, its value being related to the melting-point of its fatty acids. It is calculated that the palm oil placed on the market (that is, exclusive of the large amounts consumed where produced), amounts to 70,000 to 80,000 tons per annum. Before the European War, the price varied with the year from 20*s.* to 26*s.* per cwt. The best qualities of palm oil are from Lagos; then come those of Old Calabar, Benin, and Acora; while among the more impure varieties are those from Gabun, Liberia, and the Cameroons.

PALM-NUT OIL (or Palm-kernel Oil) is obtained by crushing and then either pressing in hydraulic presses or extracting with solvents the stones contained in the fruit of the West African palm (*Elais guineensis*); freed from shell, the seed forms 9 to 25 per cent. of the weight of the fruit and contains 43 to 55 per cent. of fat, which is white or straw-coloured and free from fatty acids when fresh, although it turns rancid fairly easily in the air; it melts at 26° to 30°.

It consists of about 15 to 25 per cent. of triolein, 33 per cent. of triglycerides of stearic, palmitic, and myristic acids, and about 45 to 55 per cent. of triglycerides of lauric (in preponderance), capric, caprylic, and caproic acids.

It bears a great resemblance to coconut oil, even in the property of its soaps of taking up large proportions of water—as much as 600 per cent. (coconut soap up to 1200 per cent.)—and of being somewhat soluble in solutions of salt. The total quantity of palm nuts placed on the market is about 1,125,000 tons.

COCONUT OIL (or Coconut Butter) is obtained from the coconuts yielded twice a year by the palms *Cocos nucifera* and *Cocos butyracea*, which grow abundantly in Africa, Ceylon, Cochin China, and the Indies.

The coconut is oval (Fig. 288) and about 20 to 25 cm. long and 12 to 16 cm. broad; it is covered with a fibrous mass, used for making matting, cord, and baskets, and with a hard, woody shell, 8 to 12 mm. thick, which some time before maturation contains a sweetish, watery liquid (*coconut milk*), this subsequently disappearing and giving place to a soft edible pulp. The latter hardens in the air and is sold under the name of *copra*

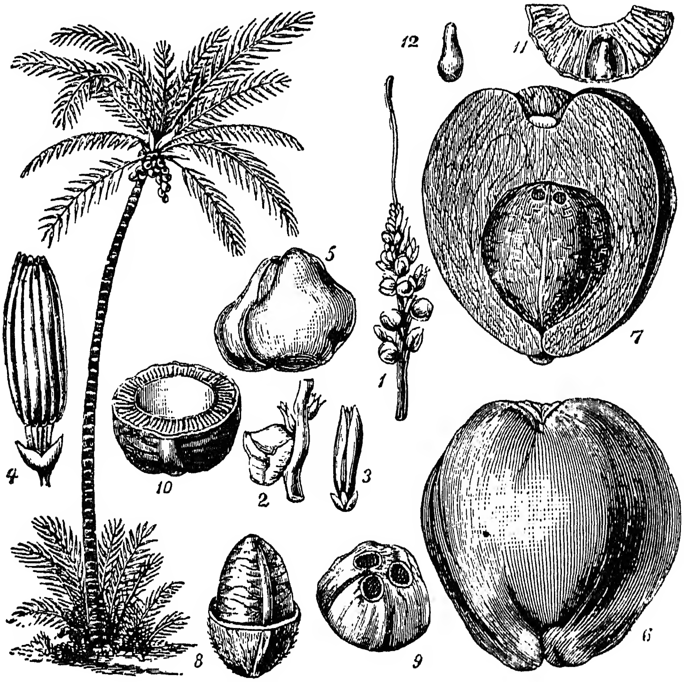

FIG. 288.—*Cocos nucifera.*

1, flowers; 2, round female flower and two male flowers; 3, male flower; 4, male flower, separated from leaves and calyx, magnified; 5, female flower, separated from leaves and calyx, magnified; 6, fruit; 7, same in longitudinal section, the bony seed being surrounded by a fibrous layer; 8, the seed with one-half of the fibrous layer removed; 9, the bony seed with three orifices; 10, section of the inner seed with chamber filled with latex; 11, lower portion of the husk with the embryo; 12, embryo.

(60 to 70 per cent. of oil) for the extraction of oil. At the place of production this is carried out in a very primitive manner, but in European factories the dry pulp is ground, steeped in boiling water and pressed, first cold and then hot.

The oil is nowadays decolorised with bone-black or absorbent earths (magnesium hydrosilicates), and in the white form thus obtained is used as a comestible (*coconut butter*; *see* Margarine), after the free acids have been removed with highly concentrated solutions of caustic soda and after the odorous constituents have been expelled by means of superheated steam. The best form for use as food is the softer, almost liquid butter obtained by the first pressing in the cold. Its digestibility is equal to that of margarine and butter. If it contains more than 2 per cent. of free fatty acids (expressed as oleic acid), it cannot be used for food and then goes to the soap factory as industrial coconut oil.

Its composition is variable, and of the unsaturated acids it contains only oleic acid (about 10 per cent.), while glycerides of myristic and lauric acids are present in large quantities and those of caproic, caprylic, and capric acids to the extent of 2 to 3 per cent.

The pure fat contains no free fatty acids, or at most traces. It has already been mentioned that it gives a soap separable from solution only by very large quantities of salt; it is, however, capable of absorbing as much as 10 to 12 times its own weight of water, and is hence highly valued by soap manufacturers. It is used alone for culinary purposes and for mixing with margarine and adulterating cacao butter.

In its analysis, attention is paid to the physical and chemical constants given in the Table on p. 466.

A large area of the earth's surface (about 1,400,000 hectares) is under coconut palms, which in a good year would yield 960,000 tons of coconut oil.

VEGETABLE TALLOW (Chinese Tallow) is obtained by pressing the fruit (separated more or less from the seeds) of *Stillingia sebifera* (*tallow-tree*), which grows in China, Indo-China, etc. Pressing of the seeds (3 per fruit) yields *stillingia oil*, which is to some extent drying (iodine number more than 135). The tallow, however, serves well for making soap and has an iodine number of about 30, but this varies somewhat owing to variation of the amount of stillingia oil present. The tallow melts at 35° to 44°, and is sold in 40- to 50-kilo cakes wrapped in straw.

COTTONSEED OIL is obtained by pressing the shelled, washed seeds of the cotton plant (*Gossypium herbaceum* and *barbadense* cultivated in North America, and *G. religiosum*, *hirsutum*, and *arboreum*, cultivated in Egypt, India, China, Siam, etc.). The whole cottonseed, with the husk, contains 7 to 10 per cent. of water, 15 to 20 per cent. of nitrogenous substances, 18 to 22 per cent. of oil, 15 to 23 per cent. of cellulose, 24 to 30 per cent. of non-nitrogenous extractive matter, and 3·5 to 4·5 per cent. of ash; the decorticated seed contains 28 to 38 per cent. of oil. About 1 per cent. of down remains adherent to the husk (45 per cent. of the weight of the seed), and this is separated to make cotton wool, paper, and nitrocellulose.

The whole, or decorticated, seeds are ground and the flour pressed at 100° in hydraulic presses in two or three stages. The pressed cake is used as fodder or as fertiliser, and contains 3 to 9 per cent. of oil and 15 to 30 per cent. of nitrogenous matter if from the whole seeds, or 8 to 20 per cent. of oil and 35 to 50 per cent. of nitrogenous matter if from decorticated seeds.

The crude oil is reddish-brown (sulphuric acid produces a red coloration) and is decolorised by stirring with 6 to 10 per cent. of caustic soda solution of 10° to 15° Bé. and passing through it a vigorous current of air, first in the cold (40 to 50 minutes) and then when heated to 50° to 55° by indirect steam. It is then allowed to settle, and is afterwards washed with 10 per cent. of salt water (at 10° Bé.) to remove the last traces of soap, decanted off, and passed through filter-presses to obtain it clear and of a fine straw-yellow colour. It may be bleached also by heating it to 70° with 10 per cent. of fuller's earth and 1 per cent. of salt. The fatty acids separated from the glycerides of cottonseed oil contain about 26 per cent. of oleic acid, 47 per cent. of linolic acid (the oil is hence partly drying), and about 24 per cent. of saturated fatty acids (palmitic and up to 3 per cent. of a hydroxy-acid), besides a small proportion of an aldehydic substance (to which Becchi's reaction is due). It contains also 1·5 per cent. of a non-saponifiable sulphur compound and apparently a chloro-compound.

Tests for the detection of cottonseed oil in other oils have already been described (p. 492), and the analysis of the oil is carried out with reference to the constants given on p. 466.

About two-thirds of all the cottonseed oil is used directly or indirectly (as adulterant) as food; the remainder (second and third qualities) serves, with palm oil and coconut oil, for making white soaps, although in some cases it gives rise, after some time, to yellowish spots.

The total output of cottonseed should be about double that of the cotton produced. The United States produced 6,997,000 tons of the seed in 1911 and 6,104,000 tons in 1912, the output of the oil being 800,000 and 750,000 tons respectively in the two years.

KAPOK OIL. This oil, obtained in 25 per cent. yield by pressing kapok seeds (from *Eriodendrum anfractuosum*, growing in Java, East Africa, the Antilles, and Central America), exhibits slight drying properties and has the specific gravity 0·920, iodine number 95 to 115, and saponification number 180 to 195. The crude oil has an acrid odour and a repulsive taste, but the refined product is insipid and odourless and is used mostly for making soap. With Becchi's reagent it gives an intense reddish-brown coloration, and with Halphen's reagent a pale red colour.

MAIZE OIL (in America, **Corn Oil**) is now prepared in large quantities in America and

Italy from maize germs, which are separated during grinding. These germs contain 40 to 50 per cent. of oil, and after being pressed hot leave an excellent cake for cattle-food (5*s.* to 6*s.* per cwt.). The dense oil has a fine golden yellow colour and a faint odour of maize, and serves well for soap-making and for adulterating edible oils and linseed oil. That obtained by extracting the dried grains from spirit manufacture (*see* p. 182) is reddish brown, and is used for burning and as a lubricant when mixed with olive and mineral oils, but is not used alone, as it tends to resinify. As a drying oil it has no great value.

The fatty acids of the glycerides of maize oil are: stearic and palmitic (4 to 25 per cent.), oleic (about 40 per cent.), linolic and linolenic (about 45 per cent., so that the oil is partly a drying one), and small proportions of arachic, hypogæic, caproic, caprylic, and capric acids; the oil contains also about 1·2 per cent. of lecithin and 1·4 per cent. of non-saponifiable substances, mostly cholesterol, or, more precisely, *sitosterol*, identical with that obtained from wheat and rye.

If in North America (Illinois) alone the oil were extracted from the germs of all the maize produced (about 6,000,000 tons—the world's total production being over 7,500,000 tons, 900,000 of this in Italy), more than 250,000 tons of the oil should be obtained, but only about 40,000 tons of maize oil are produced at the present time, about one-half of it being exported.

SESAMÉ OIL (Gingelly Oil, Teel Oil) is obtained from the seeds of *Sesamum indicum* (brown, oval, flat seeds, 4 mm. long, 2 mm. broad, and 1 mm. thick: Fig. 289) and of *Sesamum orientale* (violet-brown or black), the latter giving as much as 50 per cent. of oil when pressed once in the cold and twice hot. The first oil expressed serves as a food for 250 millions of the inhabitants of India, where the area under sesamé exceeds ten millions of acres (*i.e.*, 4,000,000 hectares). The exportation of sesamé seeds from India amounts to about 120,000 tons annually, nearly all of this being directed to the Marseilles market, whence other countries are supplied. The Levant produces about one-tenth as much as India, and a little is produced in Africa, China, and Japan. In France the sesamé oil industry is declining owing to the obstinate empiricism of the older manufacturers and to the almost prohibitive Customs duties of various countries, but more than 1000 truckloads of the oil are still exported per annum.

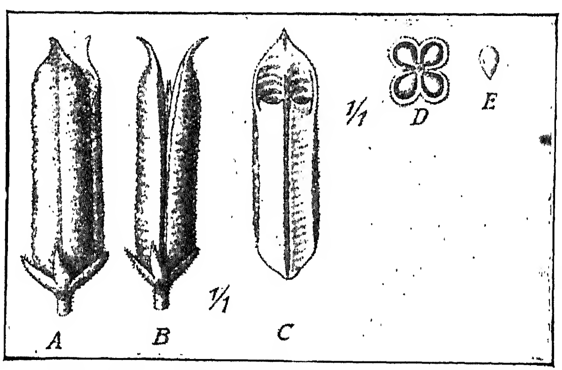

FIG. 289.—*Sesamum indicum*, with white seeds.

A and *B*, ripe fruit seen from the front and side; *C*, longitudinal section of fruit; *D*, transverse section of the fruit and four rows of seeds; *E*, seeds. All natural size.

Sesamé cake (dark or pale), so largely used as cattle-food, has the composition: water, 10 to 12 per cent.; protein substances, 37 to 39 per cent.; fat, 9 to 10·5 per cent.; and ash, 9·5 per cent.

Sesamé oil has a golden-yellow colour, that from the Levant being the paler; it consists of glycerides of stearic, palmitic, oleic, and linolic acids, 78 per cent. of the fatty acids being liquid with an iodine number of 140. The physical and chemical constants are given in the Table on p. 466, and the characteristic reactions for detecting it when mixed with other oils on p. 492. It is dextro-rotatory (+ 0·8° to + 2·4°).

The characteristic reactions, especially the colorimetric ones, are due to special components, such as *sesamin*; a lævo-rotatory alcohol, *sesamol*, $C_{26}H_{44}O, \frac{1}{2}H_2O$, which gives Baudouin's reaction (p. 472), and the methylene ether of hydroxyhydroquinone, $C_7H_6O_3$.

Sesamé oil is used in the manufacture of oleomargarine and soap and as burning oil.

ARACHIS OIL (Earthnut Oil, Peanut Oil) is obtained from the seeds of *Arachis hypogæa*, cultivated as a herbaceous annual in Africa (largely in Senegambia and in less degree in other parts), India, United States, Java, Sumatra, the Philippines, Japan, Formosa, the Plate, Southern China, Indo-China, and to some extent in Spain, the south of France and Italy.

The fruit develops in the ground and attached to the roots, and consists of a yellow fibrous husk containing two seeds covered with a reddish-brown skin (Fig. 290). Senegal seeds contain about 14 per cent. of water, 48 per cent. of oil, 25 per cent. of nitrogenous substances, 3 per cent. of cellulose, and 2 per cent. of ash; the African seeds contain up to 50 per cent. of oil, the Indian 44 per cent., and the American 42 per cent.

The toasted seeds, which are consumed as a fruit, readily turn rancid and acquire a repulsive flavour, and are usually eaten immediately after toasting. Large quantities of the nuts prepared in this way are consumed in America, while considerable amounts are also ground, converted into a paste and slightly salted (4 per cent.) to make *peanut butter*. Before the War the nuts were sold in the husk at 10*s*. to 12*s*. per cwt. and the dehusked nuts at 16*s*.

The ground, dehusked nuts yield about 30 per cent. of oil at the first cold pressing, 7 to

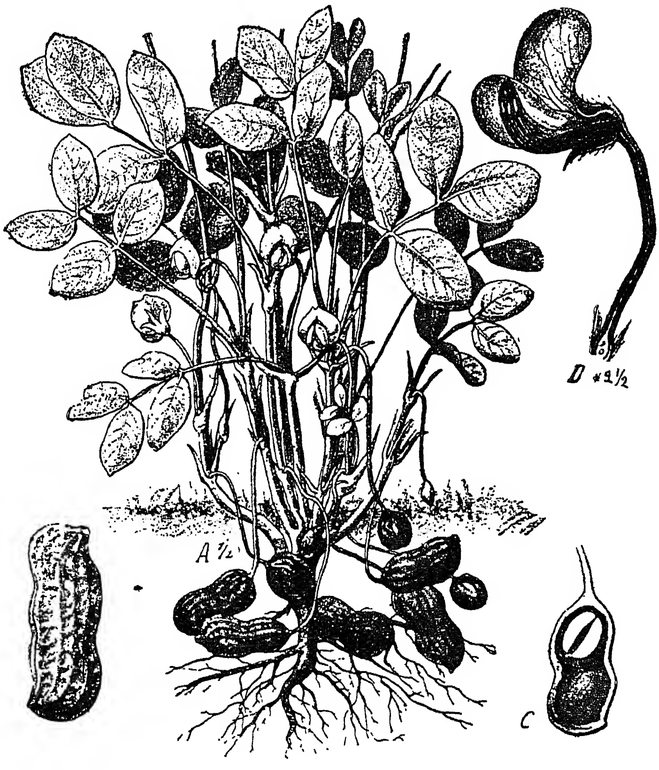

FIG. 290.—*Arachis hypogæa.*

A, whole plant (one-third natural size) with fruit; *B*, fruit (three-fourths natural size); *C*, fruit open, with one seed cut; *D*, separate flower (double natural size).

8 per cent. at the second cold pressing, and about 7 per cent. at the third pressing when hot. The oil obtained by the first cold pressing is almost colourless, has a slight flavour of beans, and is largely used as a comestible and for adulterating olive oil, although it readily turns rancid. The second pressing in the cold gives burning oil, and the third, in the hot, oil for soap-making. Arachis cake causes abortion in cattle. The liquid components contain *triolein* and *trilinolein*; the presence of hypogæic acid is uncertain; the solid constituents are composed of triglycerides of lignoceric acid, and to a less extent of arachic acid (5 per cent. of the oil). In olive oil arachis oil is detected by Renard's test, as modified by Tortelli and Ruggeri and by Fachini and Dorta (*see* p. 492).

COLZA OIL. This is obtained by pressing the seeds of *Brassica campestris* which is grown in France, Belgium and Germany, although most of the seeds come from India. The seeds are reddish-yellow and contain 5 to 7 per cent. of water, 4 to 6 per cent. of ash, 6 to 15 per cent. of cellulose, 19 to 22 per cent. of nitrogenous substances, and 38 to 45 per cent.

of oil (the Indian seeds are the richest, but contain also more sinigrin and myrosin, which give mustard oil with water, so that the cake is not utilisable as cattle food).

The *ravison*(*Brassica napus*) yields the brownish-yellow ravison oil, with an unpleasant taste and penetrating odour; its colour and taste are improved by refining by means of concentrated sulphuric acid, zinc chloride, etc. The oil consists of glycerides of oleic, erucic, stearic and arachic acids, with 1 per cent. of phytosterol. It is used for illuminating purposes, as it gives a bright, non-smoky flame; it serves also for making soft soap and, when heated to a high temperature in a current of air, yields a viscous product (oxidised oil). Rubber substitutes are obtained by heating it with sulphur or sulphur chloride.

SOJA BEAN OIL (Chinese Bean Oil) is extracted from the beans of *Soja hispida* (or *Soja japonica* or *Phaseolus hispidus*), which are cultivated in China and Japan (Formosa). The crushed beans are heated in jute bags over jets of steam and then pressed. A large part of the oil is used for soap-making. After purification by standing, the oil has the sp. gr. 0·9255 at 15°; acidity, 0; saponification number, 193·2; iodine number, 135; Hehner number, 95·95; Reichert-Meissl number, 0·45; Maumené number, 86 to 87; index of refraction, 1·4750 at 20°; solidification point, — 8° to — 16°; melting-point of the fatty acids, 27°; and solidification-point of the fatty acids, 22° (Oettinger and Buckta, 1911). The exportation of the oil from China amounts to 60,000 tons per annum.

GRAPESEED OIL. The seeds of the grape contain 10 to 20 per cent. of oil (more in white and sweet grapes). They are separated from the skins by drying in the sun or in ovens and then beating, the sun-dried seeds containing 10 to 12 per cent. of water, 9 to 12 per cent. of carbohydrates, 10 to 11 per cent. of nitrogenous matters, and 2·5 to 4 per cent. of ash. The sieved seeds are dried completely, ground, steeped in 10 per cent. of water, heated, and pressed; the cake is broken up, treated with 20 to 25 per cent. of water, and pressed again, this treatment being repeated so that all the oil may be extracted. The oil can also be extracted by means of solvents (benzine or carbon disulphide). When dark-coloured (extracted from the seeds of distilled marc or in the hot with solvents), it can be readily decolorised with animal-black or fuller's earth. It has not a very pleasant odour and is rather bitter (if expressed in the hot). Pressure of the seeds yields 9 to 13 per cent. of oil.

This oil consists of glycerides mainly of linolic acid, together with those of solid fatty acids (10 per cent.), and a little erucic, linolenic, and ricinoleic acids. It has the sp. gr. 0·9202 to 0·9350.

It has slight drying properties and solidifies between — 10° and — 15°; its saponification number is 178 to 180; iodine number, 130 to 140; Wollny number, 0·46; Maumené number, 52 to 54; and butyro-refractometer reading, 60 at 40°. The acetyl number of the fatty acids varies from 43 to 144, according to the extent of oxidation; it thus resembles castor oil to some extent, so that it is recommended for the manufacture of sulphoricinate (*see* p. 390).

The pure oil expressed in the cold is used as a food, and the other varieties for soap-making, but if purified with sulphuric acidi t serves well as a lighting oil, not so much on account of its luminosity, which is rather low, but more especially because it gives a smoke-less flame.

After the removal of the fat, the *cake* contains 10 to 15 per cent. of water, 14 to 18 per cent. of protein substances, 6 to 18 per cent. of fat, and 6·5 to 7 per cent. of ash, and is used as cattle-food and also as a fuel.

In Italy the extraction of grapeseed oil is capable of considerable development. A few oil-crushing mills of Southern and Northern Italy treat a certain amount of the seed. Seeds obtained from distilled vinasse are of less value, as they yield an inferior, brown oil.

TOMATOSEED OIL. Dried tomato seeds [1] contain 18 to 22 per cent. of oil, two-thirds

[1] Tomatoes are the fruit of a herbaceous plant (*Solanum lycopersicum*) of Peruvian origin, and from 1700 to 1850 were cultivated in various countries as a garden plant for local domestic use. Since 1860 they have been grown extensively in North America, especially in California, where in 1911 15,000 tons were marketed, large quantities being exported to other countries in the fresh condition. In Italy also they are cultivated on a large scale.

Fresh tomatoes contain 92 to 95 per cent. of water, 1 to 3 per cent. of skin, 2 to 5 per cent. of seeds, 0·9 per cent. of nitrogenous compounds, 0·2 per cent. of fat, 2·5 per cent. of sugars, 0·8 per cent. of cellulose, 0·6 per cent. of ash, and 0·4 per cent. of free acids (mostly citric).

Concentrated *tomato preserve* is prepared by rupturing the fresh fruit, centrifuging and hydraulically pressing the mass, and concentrating the whole of the liquid in vacuum pans

of which is extracted by subjecting the ground seeds to a pressure of 300 to 400 atmos. The residual *cake* forms an excellent cattle food (superior to linseed cake), as it contains 36 to 38 per cent. of proteins, 10 to 12·8 per cent. of fat, about 30 per cent. of non-nitrogenous extractives, 8 to 10 per cent. of water, 6 per cent. of cellulose, and 5 per cent. of ash.

The oil expressed in the cold from sound seeds is straw-yellow, and with 20 per cent. of tallow gives a good washing soap.

Analysis of the oil gives the following results (Fachini): density at 15°, 0·9215; refractive index, 1·4765; acid number, 0·46; saponification number, 191·6; iodine number, 114; iodine number of the fatty acids, 122·7; iodine number of the liquid fatty acids, 142·2; Hehner number, 93·8; acetyl number, 20·4.

WOOD OIL (from Japan and China) is derived from the seeds of *Aleurites cordata*. These contain as much as 53 per cent. of oil with an odour like that of castor oil and yield 42 per cent. when pressed cold; the oil has the specific gravity 0·936 to 0·943, and the iodine number 155 to 166, and exhibits drying properties. At 250° it sets to a solid, transparent, elastic mass, and it is used for making paint and for rendering wood and fabrics impermeable.

TREATMENT OF FATS FOR THE MANUFACTURE OF SOAP AND CANDLES

Candles are mostly made from solid fatty acids (stearic and palmitic) obtained by decomposing fats and oils into glycerine and fatty acids and pressing from the latter the liquid fatty acids, which are used, either alone or together with the solid acids, for soap-making. Liquid oils and soft fats, which contain little stearic and palmitic acids, are hence used not for candles but only for soap, but the stiffer fats are often treated in one and the same works for making candles and soap.

The resolution of fats into acids and glycerine is carried out in very varied ways: by means of lime, sulphuric acid, or superheated steam, or by biological or catalytic methods.

(1) Saponification with Lime and Separation of the Solid Fatty Acids. Theoretically 100 kilos of fat (*see* p. 467) require 9·5 kilos of lime for hydrolysis, but when this process was first used industrially by Milly in 1834 as much as 15 per cent. of lime was used, so that a very large amount of sulphuric acid was consumed in liberating the fatty acids from the calcium soaps formed, while fatty acids were carried down by the enormous quantities of calcium sulphate formed and hence lost.

On this account the process was not used, but Milly showed later (1855) that, by heating in an autoclave under pressure instead of in open pans, the amount of lime could be reduced to 2 to 3 per cent.—that is, less than the theoretical quantity—and yet practically complete saponification effected (*see* p. 457). Indeed, after one hour 64 per cent. of the fat remained unsaponified; after two hours, 24 per cent.; after four hours, 15 per cent.; after six hours, 9 per cent.; after nine hours, 2 per cent.; and after 12 hours, 0·7 per cent.

Fig. 291.

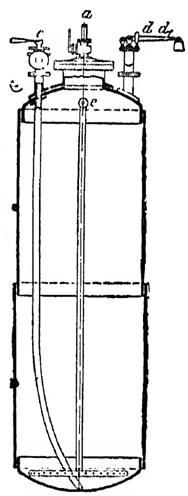

Fig. 292.

The saponification is now carried out in large vertical copper autoclaves (Fig. 291) (5 to 6 metres high, 1 to 1·2 metre in diameter, of sheet copper 15 to 20 mm. thick), into which are passed several cwts. (up to 2 tons) of the fused fat from the tank, *A* (Fig. 293),

(*see* chapter on Sugar) until a red pulp or sauce containing about 60 per cent. of water is obtained. This is mixed with 2 to 3 per cent. of salt and either bottled or sealed in cans after being sterilised at 100°.

The pressed *residues*, amounting to 7 to 9 per cent. of the weight of the original fruit, contain 6 to 8 per cent. of skin, 22 to 24 per cent. of seeds, and about 60 to 70 per cent. of water, and readily putrefy. Nowadays they are broken up immediately they come from the presses, and are then dried and beaten while hot to separate the skins from the seeds.

and then about one-third as much milk of lime, containing 2 to 3 per cent. of lime (calculated on the fat), from the vessel *B*. The heating is continued for six to eight hours at a pressure of 8 to 10 atmos., steam free from air being passed in, first at low pressure from the boiler, *D*, and then at high pressure (10 to 12 atmos.) by the tube, *e* (Fig. 292), reaching to the bottom of the autoclave and terminating in a perforated coil. The steam alone

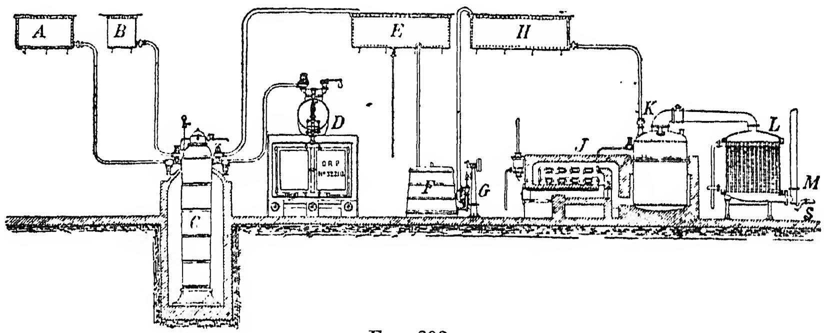

FIG. 293.

keeps the mass mixed without the special stirrers formerly used, if the precaution is taken of allowing a little steam to escape continually from a valve at the top. At the end of the operation the steam is shut off, and when the temperature has fallen to 125° to 130° (about 3·5 atmos. pressure) the internal pressure is utilised to discharge first of all the aqueous glycerine from below by opening the valve, *c*, connected with a tube reaching to the bottom of the autoclave. In a similar manner the fused and subdivided calcium soap mixed with free fatty acids is forced into the tank, *E*, where a further quantity of aqueous glycerine separates, or the calcium soap is passed directly to the lead-lined vessels, *F*, where it is decomposed by a sufficient quantity of sulphuric acid to neutralise all the lime added.[1] After shaking, the gypsum is deposited and can be separated, and the fatty acids, which float, are washed several times with hot water, and then, if the fatty acids are distilled—as is done in certain factories where dark fats are treated—they are forced by a pump, *G*, to the tank, *H*. The latter feeds a cast-iron or copper (this is considerably attacked) boiler, *K*, which is heated partly by almost direct-fire heat and partly by superheated steam (at 180° to 230°) passed into the interior from the superheater, *J*. The steam carries the fatty acids, which distil, into the tinned copper condensing coil, *L*; these acids finally collect in a white condition, together with condensed water, in *S*, while the non-condensed gases are evolved from the tube, *M* (*see* later: Decomposition with Sulphuric Acid).

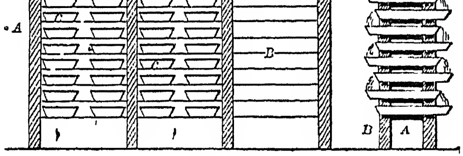

FIG. 294.

Where the fatty acids are not distilled, they are solidified by passing them into a number of superposed tin-plate pans (Fig. 294) fed by the tubes, *D*, from the fused fatty-acid tank, *F*. When all the pans are full, the tubes, *D*, are closed with wooden plugs, *E*, and in 24 hours many of the pans

[1] During recent years several factories have replaced the lime by *magnesia* (calcined natural carbonate), which possesses various advantages: when it is used in the proportion of 1·5 to 2 per cent., a pressure of 4 to 5 atmos. is sufficient to produce complete saponification, since the magnesium soap formed gradually emulsifies and almost dissolves in the remaining fat, which is thus easily resolved by the water and magnesia. Then, too, decomposition of the magnesium soap with sulphuric acid, instead of giving an insoluble and useless salt (calcium sulphate, which always retains a little fat), gives magnesium sulphate, which is soluble in water, readily separable by simple decantation and in some cases utilisable. For similar reasons, *zinc oxide* is now used in some of the Italian factories. Bottaro (1908) has suggested the use of sulphurous anhydride to decompose the calcium soap from the autoclave.

contain solid cakes, consisting of a mixture of solid stearic and palmitic acids and liquid oleic acid. In order to separate the latter, the cakes are wrapped in woollen or camel hair or goat's hair cloths and are then placed between metal plates and pressed, first in the cold with a pressure gradually increasing to 200 to 260 atmos. A second pressing at 40°, either in the same press or in a horizontal press, results in the almost complete separation of the oleic acid, which, however, retains in solution a little palmitic and stearic acids. The latter acids are separated by cooling the oleic acid and, after some time, filtering or decanting off the *oleine* (p. 358), which is then put on the market or used for soap making.

The solid white cakes of stearic and palmitic acids, freed from the dark edges, bear the commercial name of *stearine* and melt at 56° to 56.5°. These are often melted again, washed with warm water, poured into pans to solidify, and then pressed hot in hydraulic presses so as to remove the final portions of oleic acid; this product, known as *double stearine*, melts at 57.5° to 58°.

The solidification of the crude acids, after liberation by sulphuric acid, is now effected more rapidly and more perfectly by passing the fused acids at *g* (Figs. 295 and 296) into a casing into which dips a large, rotating, double walled cylinder. Between the walls flows a non congealing solution like that from an ice machine (*see* Vol. I., pp. 259, 621), and the layer of fatty acid solidifying at the surface is detached by means of a scraper, *h*, and falls into a cooled box, *F*, connected with the pump, *P*, and functioning as a filter press. This process of the firm of Petit Frères has now been improved by replacing the cylinder by a highly cooled toothed wheel. In some cases, also, channelled cylinders are used, whilst in others the liquid fatty acids are withdrawn from the cold pasty mass containing the mixture of liquid oleine and the stearine in small crystals, by immersing in the mass a rotating vertical cylinder formed of metallic gauze and covered with a well stretched cloth; inside the cylinder the pressure is reduced by means of a suction pump, so that the liquid oleic acid is sucked in, while the stearic acid is gradually scraped from the surface of the cylinder and pressed in a hydraulic press.

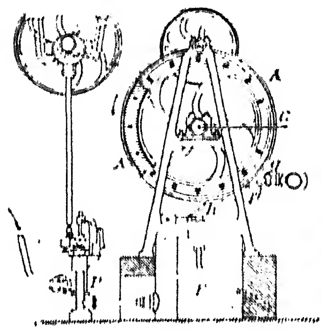

FIG. 295.

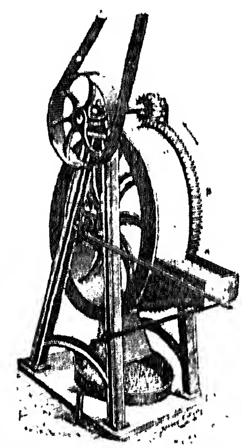

FIG. 296.

Messrs. Lanza Bros. of Turin, instead of separating the liquid from the solid fatty acids by means of hydraulic presses, suggest emulsifying and dissolving the liquid acids with solutions of sulpho oleic acid, so that they separate at the surface, while crystals of the solid fatty acids collect underneath (Ger. Pat. 191,238). The sulpho oleic acid is prepared by shaking 100 parts of oleic acid with 50 parts of sulphuric acid of 66° Bé. in the cold and then diluting with 4000 parts of water.

The decomposition of fats by lime in an autoclave at not too high a pressure has the advantage of giving the fatty acids in a sufficiently clear condition to render distillation unnecessary; the resulting glycerine and stearine are also clear.[1]

[1] During recent years, industrial application has been made of the **Krebitz process** (Ger. Pat. 155,108, 1902), which is a simplification of the lime process with direct production of soda soap, and is attended by considerable saving in fuel, caustic soda, and plant. To the fused fat is added the necessary quantity of lime (10 to 12 per cent. CaO) mixed to a paste with three to four times its weight of water, the mass being well mixed, boiled for five minutes, covered, and allowed to stand overnight. By this means saponification is completed and a calcium soap is obtained which can be readily ground up in a mill. When this is washed in a vat with a perforated bottom, the first portion of hot wash-water removes the major part of the glycerine as a solution of 10 to 20 per cent. concentration, while a second washing gives a more dilute glycerine solution which is used for the first washing of the calcium soap of a subsequent operation. When treated in the hot with sodium carbonate solutions, the calcium soap yields soda soap and calcium carbonate, which require skilled manipulation for their proper separation. In this case also, fusion and treatment with hot water is employed for the complete removal of impurities. This process is not applicable to the manufacture of soft soaps.

(2) **Decomposition with Sulphuric Acid** (proposed by Achard in 1777 and by Frémy in 1836). This method is now used more especially for very dark fats, which should, however, be freed from impurities, dried by fusion at 120°, and decanted after long standing. The fused fat is introduced into a double-walled, lead-lined, copper or iron boiler fitted with a hood for carrying off the sulphur dioxide which is always evolved. According to the nature of the fat, it is heated with 5 to 10 per cent. of concentrated sulphuric acid at 120° for 1 to $1\frac{1}{2}$ hours, steam being passed through the jacket and the mass kept mixed by a current of air passing through it. The operation is finished when a test portion, placed on a dark plate, crystallises on cooling; the mass is then passed into large wooden vats and heated with water until the emulsion first formed is resolved into two layers, the glycerine below (this is separated and freed from sulphuric acid by means of lime) and the acids above. The latter is subsequently boiled several times with water until the excess of sulphuric acid is removed, the sulphuric ethers of oleic acid being decomposed with formation of solid hydroxystearic acid. The resulting fatty acids are dark, since they retain in solution the impurities of the fat partially carbonised by the sulphuric acid; to purify and whiten them, they are distilled with superheated steam, as described above (*see also* Fig. 293); the first and last portions which distil are the more highly coloured and these are redistilled. Hirzel (Ger. Pat. 172,224, 1906) has devised an arrangement for continuous distillation, all that is required being a boiler of moderate size into which the crude fatty acids are run in a constant stream; the pure acids distil over, while the *tar* remaining at the bottom of the boiler is discharged.

Redistillation of this *tar* gives a final residue of black *stearine pitch*, amounting to about 2 per cent. of the fatty acids distilled. In some works the fatty acids are distilled in a vacuum at a temperature not exceeding 240°, higher temperatures than this giving a coloured product; the acroleïn and hydrocarbons given off are condensed.

The fatty acids obtained by distillation are separated into liquid and solid by pressure in hydraulic presses, liquid *distilled oleine* and white, solid *distilled stearine* being thus obtained. This oleine always contains a little acroleïn and hydrocarbons, as the crude fatty acids which are distilled invariably include a small proportion of non-saponified neutral fat. On the other hand, distillation results in the formation of an increased amount of solid fatty acids (about 15 to 18 per cent.), since sulphuric acid converts oleic acid partly into the corresponding sulphuric ether, which yields solid hydroxystearic acid, m.-pt. 84°, when boiled with water:

$$C_{17}H_{33}\cdot CO_2H + H_2SO_4 = C_{17}H_{34}\begin{cases} CO_2H \\ O\cdot SO_3H \end{cases}$$

$$C_{17}H_{34}\begin{cases} CO_2H \\ O\cdot SO_3H \end{cases} + H_2O = H_2SO_4 + C_{17}H_{34}\begin{cases} CO_2H. \\ OH \end{cases}$$

During the distillation with superheated steam, the *hydroxystearic acid* is transformed almost entirely into iso-oleic acid, m.-pt. 44° (*see* p. 359). It must, however, be borne in mind that hydroxystearic acid is not very good for making candles, as it accumulates in a fused state in the cup formed by the burning candle round the wick; further, when melted with stearic acid it tends to separate in layers instead of giving a homogeneous mass.

In order to obtain a greater proportion of solid fatty acids, some works combine these two systems of saponifying by means of lime and acid. The saponification is first carried out in autoclaves in the ordinary way, but not to completion, the acids and the remaining fat (4 to 5 per cent.) being then separated by means of sulphuric acid; the fatty acids and fat are dried and completely saponified with 2 to 2·5 per cent. of concentrated sulphuric acid at a temperature of 110° to 120° maintained for an hour. The resulting fatty acids are not distilled but are simply washed with boiling water, being thus rendered rich in solid hydroxystearic acid; this process also yields a *much* purer glycerine.

L. Fournier (Fr. Pat. 262,263) has suggested a method of increasing the amount of solid fatty acids by effecting the sulphonation with concentrated sulphuric acid in a carbon disulphide solution of the fat, the reaction then proceeding immediately without heating.[1]

[1] **Transformation of Oleic Acid into Solid Fatty Acids.** For some years (about 1877–1885) *oleic acid was converted* on an industrial scale in France and England (by the process of Olivier and Radisson) *into solid palmitic acid* by utilising Varrentrapp's reaction, according to which this change is almost quantitative on fusion with solid caustic potash (*see* pp. 350 and 359): $C_{18}H_{34}O_2 + 2KOH = H_2 + CH_3\cdot CO_2K + C_{16}H_{31}O_2K$, but the greasiness and unpleasant odour of the candles obtained compared with those made from stearine, the necessity

(3) **Hydrolysis by Hot Water under Pressure** (proposed by Tilghmann in 1854, and improved by Price in England) is but little used owing to the low yields obtained and the very high pressures required. The fat, emulsified with water, is circulated in coils arranged in a furnace so as to attain a temperature of 290° to 315°.

Direct distillation of fats with superheated steam and collection of the glycerine and fatty acids in the distillate always gives low yields.

(4) The **Biological or Enzymic Process** has been applied industrially since 1902, as a result of the work of W. Connstein, E. Hoyer, and H. Wartenburg, and is based on the observations of Pelouze (1855), of Green and of Sigmund (1890) according to which, when oily seeds are pounded with water, fatty acids are gradually liberated by the action of lipolytic enzymes (*see* p. 134). It is found that the most active enzymes are those of castor oil seeds (in which they occur to the extent of 70 parts per 1000 of fat), especially after removal of the oil, but better results are now obtained by using aqueous emulsions rich in enzymes (*extract of castor oil seeds*), but much poorer in proteins (which are harmful) and containing 60 per cent. of water, 37 per cent. of castor oil, and 3 per cent. of proteins. Other active seeds are, according to Fokin, those of *Chelidonium majus*, *Linaria purpurea*, etc. When castor oil seeds are used, a milky emulsion is obtained by crushing the seeds in presence of the necessary amount of water (50 to 60 per cent.) and is decanted off roughly from the skins and treated with 0·06 per cent. of acetic acid (calculated on the weight of fat to be decomposed subsequently). Of the seeds or the enriched extract, 50 to 80 kilos are used per 1000 kilos of fat (the maximum for fats with the higher saponification number, although tallow requires the maximum amount and a temperature of 40°). To accelerate the decomposition, 0·15 to 0·20 per cent. (on the weight of fat) of manganese sulphate (*activator*) dissolved in a little hot water is added, and if the fat contains much protein or gummy matter, it is well to clarify it by heating with 1 per cent. of sulphuric acid diluted with a little water; the last traces of this acid are then removed by repeated and thorough washing with boiling water, as they would be deleterious to the reaction. With liquid fats, the decomposition is carried out at 23° and with solid ones at 1° to 2° above the melting-point, provided however that this does not exceed 42°, since at 44° the enzymes no longer act in the desired direction; if necessary, fats with high melting-points are mixed with liquid oils.[1]

The practical working of the process is as follows (*see* Fig. 297): A leaden coil *a*, *b*, for indirect steam and a tube, *d*, for the injection of air reach almost to the bottom of a lead-lined iron boiler, *A*, with a conical base; discharge cocks, *f*, are fitted to the boiler at the

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of distilling the resultant dark acid, and the difficulty of eliminating all the acetic acid, led to the abandonment of this process. Also *de Wilde and Reychler's process for transforming oleine into stearine* by heating in an autoclave at 260° to 280° with 1 per cent. of iodine or chlorine or bromine seems to have been given up in practice since 1890, the yield being less than 75 per cent. (the combined chlorine was eliminated by heating under 8 to 10 atmos. in presence of zinc dust or iron, and then decomposing the metallic soap).

The industrial transformation of *oleic acid into solid elaidic acid* by treatment with a little nitrous acid (*see* p. 359) does not give satisfactory practical results, first because elaidic acid is not a very good material for candle-making, and also because the reaction is reversible and succeeds well only with fairly pure and *fresh* oleic acid and not with the commercial acid (partly polymerised). Max v. Schmidt treats 10 parts of oleic acid with 1 of zinc chloride at 180°, then decomposes the zinc soap by boiling first with dilute HCl and afterwards with water, and finally distils the fatty acids, which can be separated into liquid and solid by means of hydraulic presses. By this process Benedikt (1890) obtained 75·8 per cent. of *stearolactone*, $C_{18}H_{34}O_2$ (the internal anhydride of *γ-hydroxystearic acid*, m.-pt. 48°), 15·7 per cent. of iso-oleic acid, and 8·5 per cent. of other saturated acids. This method was applied in Austria, but was soon abandoned, as much of the oleine remains unaltered.

K. Hartl, jun. (Ger. Pat. 148,062, 1903), in order to avoid the browning produced by the action of sulphuric acid on the impurities of the oleic acid, does not treat the oleine directly with concentrated sulphuric acid (as had long been the custom; *see* Shukoff, Ger. Pat. 150,798, 1902), but first distils the oleic acid in steam and afterwards treats it with sulphuric acid of 58° to 60° Bé. (*e.g.*, at a temperature of 60° to 80° and using 1 mol. of sulphuric acid per 1 mol. of oleic acid); the resulting fatty acids are then washed and decolorised by heating in open pans with 1 to 10 per cent. of zinc dust at 100°, the zinc soap being finally decomposed by hot dilute hydrochloric acid. W. H. Burton (U.S. Pat. 772,129, 1904) uses a process similar to that of Fournier (*see above*), benzine or naphtha being employed as solvent and the sulphonic ethers being decomposed in solution by the direct action of steam; the final product melts at 85° to 90°, but does not mix well with paraffin wax, even when fused.

Nowadays, however, the industrial transformation of oleic into stearic acid is effected solely by catalytic hydrogenation (*see* p. 480).

[1] Dunlap and Gilbert (1911) found that, when oleic acid is treated with glycerine in presence of defatted castor oil seeds and linseed, 26 per cent. of the oleic acid is transformed into glyceride in 11 days.

bottom and at various heights. The fat, and about 35 per cent. of water heated to the desired temperature in B (*see above*) are introduced and are kept stirred by means of a current of air from the compressor, L, and the reservoir, W. The castor oil seed extract, mixed with 0·2 per cent. of manganese sulphate and 0·06 per cent. of acetic acid (on the weight of fat; the reaction starts and proceeds well if the mass is faintly acid at first) is then added, the whole being mixed for about 15 minutes so as to give a homogeneous emulsion. The vessel is then tightly covered so that the temperature may be maintained, the mass being mixed from time to time to keep it emulsified. After 24 to 36 hours, when more than 90 per cent. of the fat is decomposed, the mass is mixed and heated to 80° to 85°, 0·2 to 0·3 per cent. (of the weight of fat) of concentrated sulphuric acid (66° Bé.) diluted with one-half its weight of water being then added. The whitish emulsion soon becomes dark owing to the separation of the fused fatty acids, and when this occurs the heating and stirring are suspended and the mass left overnight. The various taps are then set in operation to separate the bottom layer of fairly concentrated glycerine, the intermediate emulsified layer (3 to 4 per cent. of the fatty acids, used for soap-making) and the clear fused fatty acids which are boiled with water to free them from sulphuric acid. Originally, when the seeds were used instead of the extract, the resulting glycerine was very dark, and it was necessary to decolorise it with bone-black (nowadays it is as good as that given by saponification with lime), while the intermediate emulsified layer formed as much as 22 per

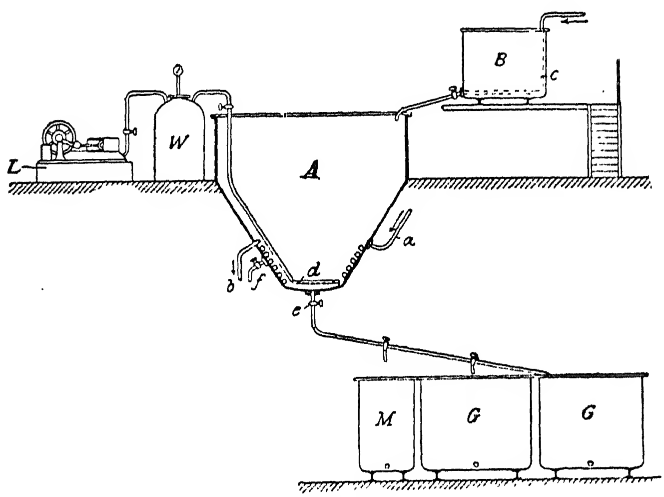

FIG. 297.

cent. of the total fatty acids (now only 2 to 4 per cent.). The *aqueous glycerine* (*sweet water*) of the enzymic process is first concentrated to 10° Bé. in open pans, the sulphuric acid being separated by means of barium carbonate in the hot. The barium sulphate is removed by filter-pressing and the filtered liquid further concentrated in a multiple-effect vacuum apparatus to 28° Bé., a clear, brownish glycerine containing only 0·2 to 0·4 per cent. of ash being thus obtained.

The biological process has spread rapidly during recent years, since the whole of the glycerine is readily recovered, while the fatty acids obtained are of far better quality than those prepared by decomposing the fat in autoclaves by means of lime, etc. The fatty acids from sulphocarbon olive oil retain, however, their characteristic green colour, and those from palm oil their orange colour. The fatty acids yielded by this process contain neither hydroxy-acids, as do those obtained under pressure, nor calcium soaps, and are hence more suitable for the manufacture of either candles or soap (*see later*, Soap).

(5) **Twitchell's Catalytic Process.** The decomposition is here analogous to that with sulphuric acid (which also, strictly speaking, is catalytic), but with *Twitchell's reagent* (*benzenestearosulphonic acid* or *hydroxystearonaphthalenesulphonic ester*) it takes place far more readily, probably because this reagent dissolves in the fat more easily than does sulphuric acid. The fats are first purified by heating to 90° to 100° in a lead-lined covered vat, A (Fig. 298), with 1·5 to 2 per cent. of sulphuric acid at 60° Bé., direct steam being

passed in so that when the acid is discharged after standing overnight it has the specific gravity 8° Bé. (for cottonseed or linseed oil, 15° Bé.). The purified fat is passed into other wooden vats, B_1 and B_2, provided with wooden covers, one half of which is removable; it is here mixed with 20 per cent. of distilled or condensed water (from the tank H), the mixture being then boiled by direct steam and 0·5 to 0·15 per cent. of the Twitchell reagent added (the minimum with pure fats and the maximum with highly impure third-grade fats). The current of steam is continued so that a homogeneous emulsion is rapidly obtained, and after being heated in this way for 24 hours about 90 per cent. of the fatty acids are liberated and the glycerine separated. No more steam is then passed through the mass, but a slow jet is kept flowing into the space between the surface of the liquid and the cover to prevent the fatty acids from turning brown during the subsequent operations owing to contact with the air. In about an hour's time, the emulsion breaks up and the fatty acids float on the aqueous glycerine; if the emulsion should not disappear, it is mixed gently for a few moments with 0·1 to 0·2 per cent. of sulphuric acid of 60° Bé. and then left. The sweet water is discharged through the separator, S, into the tank, C; it usually has the specific gravity 5° Bé. (15 per cent.) and forms 50 per cent. of the weight of the fat, and if this is not the case, the quantity of distilled water added initially and the dryness of the steam employed are varied when further quantities of fat are treated. The sweet water is neutralised with lime and concentrated in F_1 and F_2 and collected in G (*see* p. 221). For soap-making the fatty acids, which are discharged into D_1 and D_2, may be used as they are, but as a rule the saponification is completed by adding 10 per cent. of pure water and heating for 12 to 24 hours with direct steam, any small amount of emulsion formed at the surface of the liquid by the steam being destroyed by the addition of a little sulphuric acid. In this way, 97 to 98 per cent. of the theoretical amount of fatty acids is obtained. Barium carbonate (1 part per 10 parts of Twitchell's reagent used, or more if sulphuric acid were added to destroy emulsion), mixed with a little water, is now added, and the whole heated for 15 to 20 minutes; if the lower layer of water now has an acid reaction towards methyl orange, more barium carbonate must be added. The current of steam, both in and above the liquid, is now stopped, since after this the fatty acids are no longer turned brown by the air. The sweet water drawn off after clarification is very dilute and is used in place of water in the treatment of further quantities of fat. After crystallising and pressing to separate the solid from the liquid acids (*see above*), the fatty acids are now ready for converting into soap and candles. In general they are less coloured as the amount of Twitchell's reagent used and the duration of its action are diminished. Good results are not obtained until after five or six operations, by which time the surface of the wooden vessels ceases to be attacked.

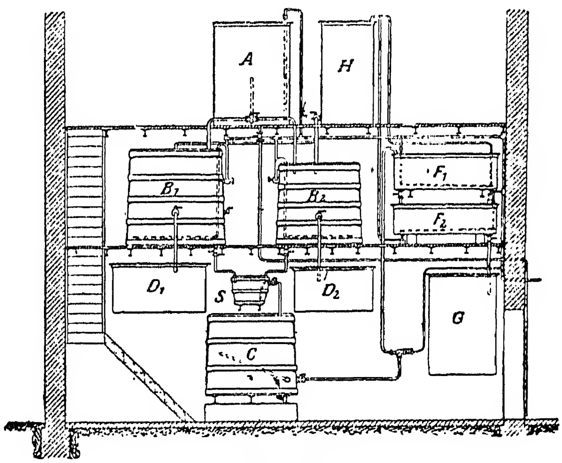

FIG. 298.

Just as with the preceding process, the use of the Twitchell process has spread considerably in America and in Europe.[1] The Twitchell reagent cost, before the War, about 1*s.* 2*d.* per kilo. A reagent, known as *Kontakt*, prepared in Petrograd in 1914, effects the scission of fats to the extent of 90 per cent. in 10 to 15 hours, and is hence three times as active as Twitchell's reagent. It was obtained by sulphonating the cyclic hydrocarbons (naphthenes) of petroleum.

[1] The plant for a factory using the biological or catalytic process is considerably less expensive than for one employing autoclaves, while there is also a decided economy in the working expenses. In the case of small plants, the cost of working increases somewhat with the Twitchell process, but there is always an advantage owing to the less initial outlay required.

MANUFACTURE OF CANDLES.[1]

The prime materials for the manufacture of candles are the combustible fatty matter and the wick.

A good candle should give a white light, should burn slowly, should not "gutter" or diffuse an unpleasant smell, should not be greasy to the touch, should be white and give a smokeless flame, and should not splutter, while the relation between the size of the wick and that of the candle must be properly chosen.

The object of the *wick* is to feed the flame regularly with the melted material. It is usually made of filaments (15 to 20) of pure cotton or linen without knots. Animal fibres should be rejected, as they give an unpleasant smell and a fused carbonaceous mass which diminishes the luminosity. Wicks formed of filaments which are only twisted require frequent snuffing, since they do not bend on themselves and do not burn completely, whilst, if they are *plaited* or woven and twisted, as Cambacères proposed, this inconvenience is overcome. For stearine candles obtained by fusion, the wick is of twisted cotton braid, while for more readily fusible materials (wax, tallow, etc.), more or less twisted wicks are used according as the candles are made by fusion or by compression. Nowadays wicks are made with suitable machines like those used for knitting, these effecting also the twisting of the filaments.

Wicks which have not been *pickled* do not act well for candles, as they leave a carbonaceous residue which diminishes their capillary property. In 1830, Milly found that the combustion of the wick is facilitated by steeping it in a solution of boric or phosphoric acid, such treatment being, however, only of advantage with braided wicks. Many other substances have since been proposed for this purpose. Thus, in France the wicks are immersed for three hours in a solution of 1 kilo of boric acid in 50 litres of water, and are then pressed, centrifuged, and dried; in some cases a *trace* of sulphuric acid is added to the bath. In Russia the wick is left for 24 hours in a solution of sulphuric acid (50 grms. per litre), squeezed, dried in hot air, steeped in a bath containing 4·5 grms. of boric acid and 18 grms. of ammonium sulphate per litre of water, and then dried. Another solution giving good results is composed of 60 grms. of borax, 30 grms. KCl, 30 grms. KNO_3, 30 grms. NH_3 and 3·5 litres of water. The borax renders the flame white.

In general these products either induce a more ready oxidation (chlorates, nitrates) or melt the ash of the wick, which thus gradually falls by its own weight. In some cases the penetration of the solution into the wick is hastened by the addition of a little alcohol.

If the candle is too large in comparison with the wick, the excess of stearine melts and forms a kind of cup with raised edges full of the fused stearine, which cannot be completely absorbed by the wick and so makes the flame smaller; then, when the edges fall, the stearine overflows and produces guttering. If, on the other hand, the wick is too large,

[1] The ancient Romans used for illuminating purposes a kind of torch steeped in wax or bitumen. Only after the second century of the Christian era was a distinction drawn between wax candles and those of tallow; the use of the latter was regarded as a luxury, while wax candles were employed in churches. The Catholic religion used them exclusively for religious functions, and thus caused a great increase in the consumption, which diminished only after the spread of the Reformation. Very soon, however, the consumption of wax candles again increased very considerably owing to their extended use at the courts of kings and princes. Meanwhile the employment of tallow candles for domestic purposes was continually spreading, and in the eighteenth century several important factories were working in England, but the candles produced were high in price and burned very quickly. Only after Chevreul's work on the nature of fats in the early part of last century (after 1815) led to improvements in the saponification and to the preparation of solid fatty acids was the rational manufacture of candles initiated. Chevreul himself, together with Gay-Lussac, patented in 1825 a process for preparing candles from stearic acid, but the resulting industrial undertakings were soon abandoned, owing to the difficulties encountered in the saponification and in the preparation of the wick. It was only when Cambacères, in 1830, devised plaited and twisted wicks, and when Milly, in 1834, introduced saponification with lime and the subsequent decomposition of the calcium soap with sulphuric acid, that the manufacture was placed on a stable and remunerative basis. Milly's first factory for stearine candles was erected in Austria in 1837, and in 1840 one was started in Berlin and another in Paris. Important improvements were made in 1842 by saponifying the fats with sulphuric acid, and in 1854 by saponifying the fats and distilling the fatty acids with superheated water or steam (processes of Tilghmann, Berthelot, and Melsen). Almost immediately after this, however, the manufacture of paraffin candles was started, paraffin wax having been obtained in large quantities by Young (1850) by the dry distillation of bituminous coal (boghead, etc.), peat, shale, lignite, etc.; this industry underwent further extension after paraffin had been extracted from petroleum and ozokerite (*see* pp. 94–104).

an insufficient quantity of wax is melted and no cup is formed to contain it, the candle guttering continually from the sides and the flame being less luminous.

In 1904 a patent was filed for the manufacture of *artificial silk* candle-wicks, which seem to give good results.

Formation of the Candles. The white blocks of stearic and palmitic acids from the presses are scraped at the surface and edges to remove adherent impurities. The purer residue is melted and shaken in a leaden vessel with sulphuric acid (3° Bé.) to dissolve and separate the impurities (iron, hairs from the press bags, etc.); the sulphuric acid is then decanted off and the stearine washed repeatedly with boiling water to remove all trace of the mineral acid. In some cases the fused fatty acids are shaken with a little coagulated albumin. In cooling, the stearine tends to crystallise, the resultant candles being then less homogeneous and more brittle. At first arsenious acid was used to prevent crystallisation, but, now that this is prohibited, the stearine is kept continually shaken until it almost solidifies when it is introduced into the moulds, and the candles then rapidly solidified. It is often more convenient to add a little white wax or paraffin wax (2 to 10 per cent.), which also prevents crystallisation of the stearine.

FIG. 299.

The quality and purity of the stearine are ascertained by the usual tests, the neutral fat being determined by Geitel's test (*see* p. 468), the paraffin wax, cerasin, cholesterol, and carnauba wax by the saponification number and by the non-saponifiable matter (*see* p. 468), and the amount of oleic acid by the melting-point (which is 56° to 56·5° for pure stearine *pressed once* and 57·5° to 58° for *doubly pressed stearine*) and the solidification point, making use of de Schepper and Geitel's Table [1] obtained by mixing saponification stearine, solidifying at 48°, with oleine having a solidifying point of 5·4°.

Candles are made in three different ways: (1) *by immersion*; (2) *by fusion*; and (3) *by pressure*.

The first of these methods is the oldest and is now almost entirely abandoned. It was employed originally for *tallow candles*, and is now sometimes used to mask the presence of inferior fat or stearine, the wicks suspended from frames being first immersed in the impure fused fat, while the outer layers are obtained by dipping into a purer fat or fatty acid.

In China considerable use is still made of tallow candles of peculiar shape with a hole in the middle.

Certain long tapers are obtained by pressure, the semi-fused wax or stearine and the wick being forced through a tube.

Almost all candles are now made by fusion in highly perfected machines, which admit of a maximum output being rapidly obtained with a minimum of labour. The moulds, which are very smooth inside, have the shape of the candles—with the pointed end below and the enlarged base at the top (Fig. 299)—and are imperceptibly conical; they are made of an alloy composed of three parts of tin and 1 part of lead. For the fusion of a large number of candles at a time (100 or more) a machine is used similar to that shown in Fig. 300. The moulds of all the candles pass through the closed metallic box, *E D*, to the bottom and cover of which they are screwed. Tepid or cold water can be passed at will through the box at *I* or *H*, so as to surround the moulds. The lower part of each

[1] *De Schepper and Geitel's Table of the solidifying points of mixtures of fatty acids:*

Temperature of solidification	Per cent. of stearine melting at 48°	Temperature of solidification	Per cent. of stearine melting at 48°	Temperature of solidification	Per cent. of stearine melting at 48°	Temperature of solidification	Per cent. of stearine melting at 48°
5·4°	0	16°	7·7	27°	21·7	38°	50·5
6°	0·3	17°	8·8	28°	23·3	39°	54·5
7°	0·8	18°	9·8	29°	25·2	40°	58·9
8°	1·2	19°	11·1	30°	27·2	41°	63·6
9°	1·7	20°	12·1	31°	29·2	42°	68·5
10°	2·5	21°	13·2	32°	31·5	43°	73·5
11°	3·2	22°	14·5	33°	33·8	44°	78·9
12°	3·8	23°	15·7	34°	36·6	45°	83·5
13°	4·7	24°	17	35°	39·5	46°	89·0
14°	5·6	25°	18·5	36°	43·0	47°	94·1
15°	6·6	26°	20·0	37°	46·9	48°	100·0

mould contains a kind of small piston which has exactly the shape of the point of the candle and can be made to traverse the whole length of the mould, being joined to an iron tube, *B*, fixed to a frame capable of being raised and lowered by the rack and pinion, *C*. All the pistons can be raised at once so as to force all the solidified candles from the moulds. In order that the wick may be always in the middle of the candle, it is wound on bobbins, *A*, and passes through the iron tube which raises the piston to the upper part of the mould. The semi-fused opalescent stearine, which is poured into the moulds kept by means of warm water (45° to 60°) at a temperature slightly above the melting-point, is then cooled by passing cold water round the moulds. When solidification is complete, the enlarged bases at the top of the candles are cut off by a knife and the candles forced out and grasped by the rods, *L*. In rising, the candles unwind from the bobbins new wicks which are thus brought into the middle of the moulds ready for the next operation. When the second batch of candles is solidified in the moulds, the wicks of the first batch are cut so as to make way for the others to be removed from the moulds. When shorter candles are required, the pistons are raised in the moulds to the desired height and the stearine then run in.

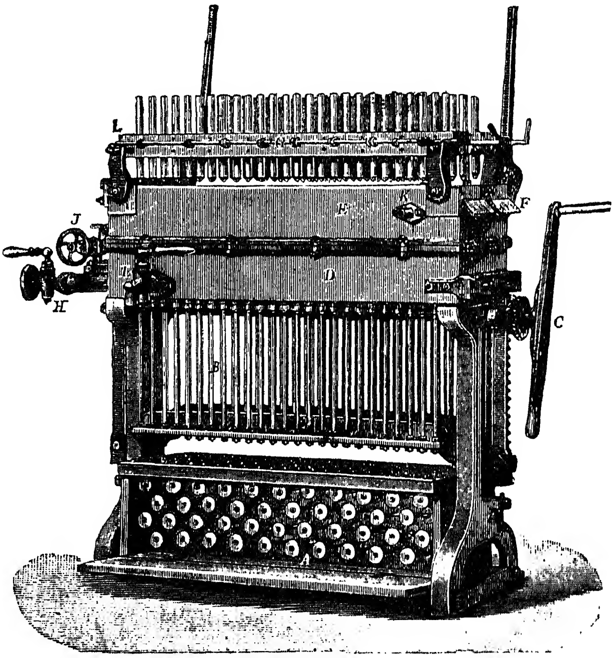

FIG. 300.

The candles thus obtained are bleached by arranging them vertically on trucks in metal gauze frames and leaving them for some days in the open air exposed to the action of the air, sunlight, and dew.

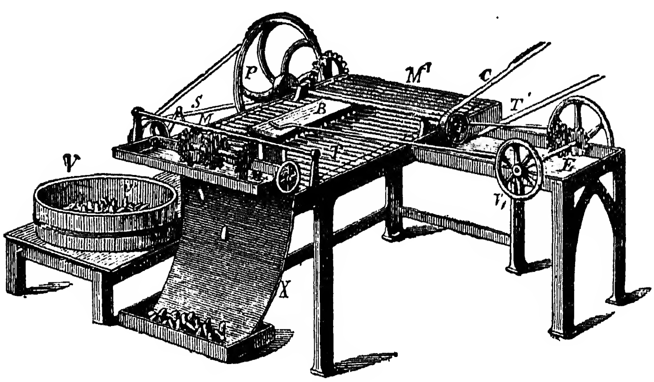

FIG. 301.

After this, the candles are washed, polished, and sawn off to a uniform length in a machine of the Binet type (Fig. 301). The candles are first dipped in a bath, *V*, containing soapy water or a dilute solution of soda, and are then placed in the grooves of the wheel, *M*, the head being against the left-hand edge, while the bases are cut off by a small circular saw, *n*; the fragments drop on to the frame, *X*, and so into the box beneath. The candles fall into the grooves of the travelling endless plane, *TM'*, and are rubbed and polished by a brush, *B*, moved eccentrically from V^1; when they reach *M'* they fall into the trough, *E*. The finished candles are stamped automatically with the trade mark and are then tied and wrapped up in packets of 12 or 24 (or ½ or 1 kilo) and placed in wooden boxes for transport.

Some factories make lighter, perforated candles, and some coloured candles or mixed candles containing wax or paraffin. To remove the semitransparency of *paraffin candles* and so make them resemble those of stearine, about 5 per cent. of stearine and 5 per cent. of paraffin oil are added. The same effect may be obtained with a small quantity of β-naphthol (Ger. Pat. 165,503) or any other substance which dissolves the paraffin wax in the hot and deposits it in the cold in a finely divided state (*e.g.*, solid fatty acids, amides, phenols, ketones, etc.). Mixed paraffin candles, containing more than 30 per cent. of paraffin wax, are now manufactured on a vast scale, wax of higher melting-point being used and the defects formerly encountered eliminated.

MANUFACTURE OF SOAP[1]

Theoretically soaps include all metallic salts of the higher fatty acids, but practically the name is given only to salts of oleic, stearic, and palmitic acids, and, in general, of the fatty acids contained in natural oils and fats. Importance attaches mainly to the sodium soaps and, to a less extent, to those of potassium and ammonium. It was at one time thought that soaps were composed largely of *margaric acid*, but it has been shown that this acid does not occur in natural fats, the confusion arising from the fact that a mixture of palmitic and stearic acids was obtained with a melting-point identical with that of synthetic margaric acid (*see* p. 350).

Almost in its entirety soap is used for washing and for cleansing and removing grease from textile fibres, sweaty garments, and the greasy, dirty epidermis of the human body, but it is sometimes employed as a subsidiary dressing in certain industrial operations, *e.g.*, in the dyeing of silk and cotton, etc.

The theory of the saponification of fats has already been discussed on p. 467, and we shall here consider the *cleansing action* of soaps. It is well known that the quantity of fat or grease that a soap is able to remove from a dirty garment is greater by far than corresponds with the amount of alkali liberated on dissolving the soap in water.

Being formed from weak acids, soap in dilute aqueous solution is undoubtedly partly hydrolysed into caustic alkali and either acid soaps in the cold or fatty acids in the hot.

[1] **History of Soap.** Soap was not known to the ancient Hebrews and Phœnicians or to the Greeks of the time of Homer, who washed their garments with the ashes of plants and water, and by mechanical rubbing. Some races used the juices of certain plants, and later it was discovered that when ashes were heated with lime they gave rise to *natron*, which was much more effective than the ashes themselves. Yet the writers of the Bible, who are certainly not conscientious and exact historians, several times mention soap, and quote the following supposed phrase of the prophet Jeremiah (who would have lived several centuries before the Christian era): "Though thou wash thee with nitre [natron] and take thee much soap, yet thine iniquity is marked before me." Seneca and Pliny mention soap in their writings and attribute its discovery to the Gauls, who prepared it from the ashes of plants and goats' fat and used it as a hair-wash and for medicinal purposes (lead plaster). It is said that Galen (second century of the Christian era) proposed the use of soap for washing. In the excavations of Pompeii has been found a complete soap factory with utensils and saponified material. Marseilles did a large trade in soap as early as the ninth century, but in the eleventh century it had a serious rival for the premier position in Savona. In the fifteenth century the industry flourished at Venice, and in the seventeenth at Genoa, which, together with Savona, Marseilles, and Alicante, enjoyed a monopoly in soap-making. In England the industry began to develop after 1650, and in Germany it assumed considerable importance after Chevreul's investigations on fats (1810–1823). With the development of the soda industry and increase of the trade in palm oil and coconut oil, the conditions in Germany and, to some extent, in other countries favoured extension of soap-making. At the present time Marseilles, although partly surpassed by the large English factories, still preserves its early fame, which, however, the Italian factories have lost. Several times in the past the renown of Marseilles has, however, been dimmed owing to the custom, even in the early days, of adulterating soap and of loading certain qualities of white soap with enormous quantities of water. This explains why, for several generations, the public preferred mottled soaps, which could not then be adulterated. It explains also the various laws promulgated in France against dishonest soap-makers, who in 1790 provoked a general protest of all the population and a petition to the deputies of the States-General from all the laundresses of Marseilles to protest "*against the adulteration of white soap and against the malefactors who adulterate it to increase its weight.*" It does not appear that things have changed greatly after the lapse of 130 years, for, since the introduction of palm oil and coconut oil in 1850, the consumer has always paid for a considerable amount of water in place of soap.

This can readily be shown by the opalescence of the dilute aqueous solutions and by the violet colour imparted to phenolphthalein by a perfectly neutral (*i.e.*, not yet dissociated) alcoholic solution or highly concentrated aqueous solution of soap, after pouring into a large quantity of water. If, then, part of the grease can be rendered soluble by the saponifying action of the alkali gradually liberated from the soap, another part is certainly carried away mechanically by the *emulsifying action* of the soap itself and of its fatty acids; this action is accompanied by the abundant production of lather, which, together with the water, incorporates and removes all the grease with which it comes into contact. It is for this purpose—the formation of lather and emulsification of the grease—that rubbing is necessary in the washing of a garment with soapy water. A mere solution of caustic soda, even in excess, does not produce a detergent effect equal to that of soap.

Soap is detergent when it dissolves in water, so that pure stearine soaps (*e.g.*, soaps from pure tallow) which are insoluble in the cold are detergent only in the hot, whereas soft soaps, consisting principally of sodium oleate, coconut, or olive oil soaps, and soluble in cold water, are detergent even in the cold.

Castelfranco (1909) considers the detergent action to be due partly to the affinity of neutral soaps to fats and fatty acids, this leading to the formation of acid soaps which yield lather, and hence result in ready emulsion and removal of extraneous substances. Thus, if an object is smeared with a thick layer of soap, it is not easy to take it away with water unless slight oiling is resorted to. For instance, hands soiled with tar or mineral oil are difficult to wash with soap and water, but if a little olive oil is first applied washing becomes easy.

According to Plateau and Hillger (1903) the detergent power, and hence the ready formation of lather, depend on the high surface viscosity of soap solutions.

Spring (1910) found that soap exercises a detergent action even on substances which do not contain fat (*e.g.*, defatted lamp-black), since these decompose the soap, forming an acid soap which agglutinates with them by absorption. Indeed, if an aqueous suspension of lamp-black is filtered, the paper is blackened owing to absorption of the black by the cellulose; on the other hand, a mixture of lamp-black with soap solution may be filtered without staining the paper, since the absorption compound of soap with lamp-black is more stable than that of cellulose with lamp-black.

As regards the molecular condition of soap in its concentrated, non-dissociated solutions, it appears demonstrated that it there exists in a colloidal condition, since an increase in the concentration is not accompanied by rise in the boiling-point, which approximates to that of water, while the electrical conductivity is minimal. According to McBain and Taylor (1910), however, in highly concentrated solutions soap is apparently not a colloid, as it conducts the electric current.

The solubility in water of almost all soaps is diminished rapidly to the point of complete separation by the addition of soluble salts which do not decompose the soap, *e.g.*, NaCl, KCl, Na_2SO_4, NH_4Cl, Na_2CO_3, and even NaOH, etc., this action being due to a change in the density of the solution and in its degree of dissociation. This phenomenon is the basis of the *salting-out* or *graining* of soap during its manufacture, but it must be noted that if the fats or fatty acids used in the making of the soap contain *hydroxy-acids*, these are almost entirely lost, as they are not separated as insoluble soaps by salting out, and mostly pass into the spent lye. Hence account is now taken of the proportion of fatty hydroxy-acids (less soluble in benzine than ordinary fats or fatty acids) present in fatty materials.

Sodium soaps are more stable than those of potassium or ammonium, since sodium salts *partly* displace potassium or ammonium from their soaps with formation of sodium soaps.

Alkali soaps are precipitated by the soluble salts of the alkaline earths and heavy metals in the form of insoluble metallic soaps. Strong acids separate the weaker fatty acids from soaps.

The alkaline soaps are usually soluble in alcohol and insoluble in ether, benzine, or benzene. Evaporation of the alcoholic solution yields a *transparent soap*.

Saponification of fats is accompanied by increase in weight, each molecule

of glyceride that decomposes fixing 3 molecules of alkali or water. A fat containing a mixture of glycerides with a mean molecular weight of 880, in reacting with 120 of NaOH (3 mols. or about 13·6 NaOH per 100 of fat), gives 92 of glycerine and 908 of water-free soap. So that theoretically 100 kilos of fat can produce about 10·5 kilos of glycerine and 102 of soap ; in practice about 1·5 to 2 kilos of glycerine is lost, while 140 to 160 kilos of soap, containing a considerable amount of water is obtained. Potash soaps are *softer* than those of soda, and soaps of liquid fatty acids *softer* than those of solid fatty acids.

Soap may be made either from the fatty acids obtained from fats by the methods described above, or from the fats themselves. In the former case the saponification is carried out mainly by sodium carbonate, and is completed (since with the carbonate it proceeds only to the extent of about 90 per cent.) by caustic soda, but in the latter case concentrated solutions of caustic soda in the hot are employed ; the carbonate is, indeed, unable to resolve glycerides, and that amount of it which always occurs in the caustic alkali is lost during the subsequent operations of salting-out, etc.

Mention has already been made (*see* p. 467) of the process of decomposing fats in an autoclave by means of ammonia and sodium chloride, which was studied by Leuchs (1859), Witelw (1876), Buisine (1883), and Polony (1882), and improved by Garelli, Barbé, and de Paoli (Ger. Pat. 209,537, 1906). This process leads directly to the sodium soap with formation of ammonium chloride, from which the ammonia may be recovered in the usual way, and, according to the above patent, gradual decomposition of the ammonia by means of steam results in a considerable separation of the *solid fatty acids* from the liquid ones, the ammonia soaps of the former being the first to decompose. Such separation can be effected also by cold water, which dissolves the ammonia soaps of the liquid fatty acids (oleates) almost exclusively (*see* also p. 467, and Note, p. 492).

In the manufacture of soaps from fats or oils, various stages are to be distinguished: (1) mixing or pasting of the fat with the alkaline lye ; (2) mixing in the hot to form the soap and separate it partially from the excess of water ; (3) *salting-out* (or "graining" or "cutting the pan") to render the soap insoluble and separate it from the lye, which thus collects under the layer of soap ; (4) *boiling* to saponify the last traces of fat, to eliminate the scum and the excess of water still remaining in the soap and to collect the latter into a perfectly homogeneous, curdy mass ; (5) the soap is often subjected to a *finishing* process, that is, a final treatment with dilute alkali hydroxide or carbonate solution, in order to separate the more thoroughly the residual impurities (aluminium or iron soaps) and so avoid a partial mottling, and to give to the soap, first, the quantity of water necessary to the particular type, and, secondly, a still more homogeneous appearance.[1]

A well-finished soap contains 35 to 40 per cent. of water and only 0·20 to 0·36 per cent. of salt and free alkali together. When excess of free caustic soda remains in the soap, considerable *efflorescence*, due to formation of sodium carbonate by the carbon dioxide in the air, occurs at the surface during the subsequent drying. In order to avoid such a serious inconvenience, it is necessary to treat repeatedly with sodium carbonate solutions, because, even if a little of the latter is left in the soap, only a slight powder forms at the surface on

[1] *Finishing* is best effected when the soap contains a certain proportion of water, namely, 10 mols. of water (40·5 per cent.) per 1 mol. of sodium oleate, or 16 mols. (48·5 per cent.) per mol. of sodium stearate. If the soap is more concentrated than this, it remains too viscous and opposes too great a resistance to the precipitation of the impurities and of the drops of saline and caustic solutions ; but if, in the finishing, the necessary quantity of water is restored (by adjusting the *concentration* of the lye), a small part of the soap dissolves, the mass becomes more liquid and, on standing, the impurities are able to fall to the bottom the more readily. Soaps which are too insoluble in the salt solution or caustic lye (colza, sesamé, linseed, poppyseed, etc.) can be finished only when mixed with readily soluble soaps (coconut, castor, etc.). On the other hand, it is necessary to prevent the soap taking up too much water, for, if this happens, it pastes together and adheres to the sides of the pan, does not transmit heat readily to the interior and hence boils with difficulty, is not easily finished and becomes uneven. Agitation of the mass and the consequent inclusion of a considerable amount of air are to be avoided, the finishing being retarded thereby. When the finishing is complete and the mass has been allowed to stand, a slight frothy layer is observed at the surface and then comes the thick layer of pure, homogeneous soap, well separated from the lye ; above this is a small, irregular, and gelatinous layer composed of more soluble soaps (of hydroxy-acids) of calcium, magnesium, and iron, and of certain other impurities insoluble in the lye (colouring-matters, coagulated proteins, etc.), and it is this mass which forms the refuse.

drying and this can be readily eliminated. In some cases, a small proportion of a non-saponifiable fat (*e.g.*, wool fat) or even of a dense mineral oil is added to the soap, the caustic soda being thereby preserved from direct contact with the air.

At one time the *coppers* used for soap-making were largely made of masonry, but nowadays they are almost universally of iron and are heated either by fire or by direct or indirect

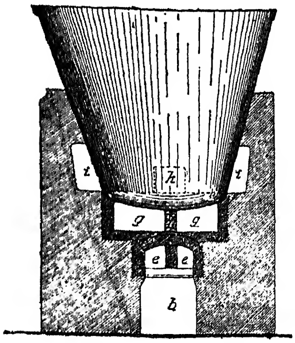

FIG. 302.

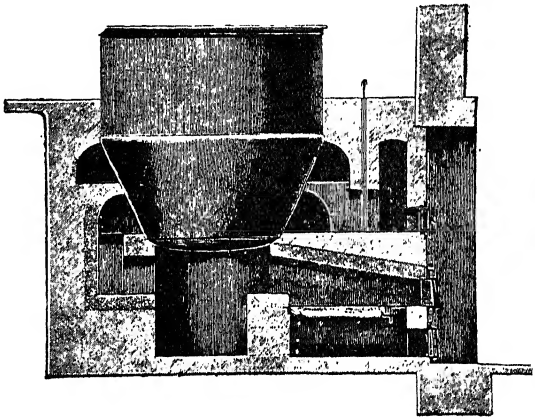

FIG. 302A.

steam, as is shown in Figs. 302, 302A, 303, 303A. Small coppers hold 10 to 50 hectols. and large ones 100 to 400.

For every 100 kilos of fat to be saponified, a copper-volume of 500 litres is taken.

In most soap-works the mixing is done by wooden blades worked by hand, although coppers are made fitted with stirrers of various forms.

The saponification of 100 kilos of fat or oil requires theoretically about 136 kilos of

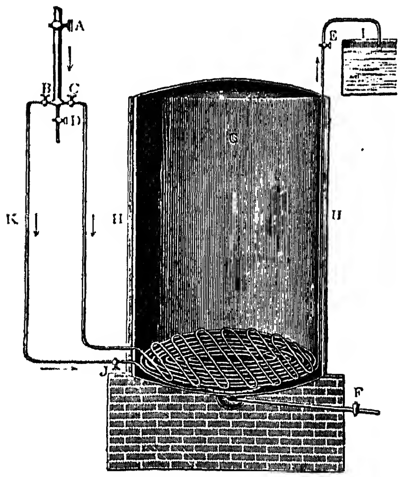

FIG. 303.

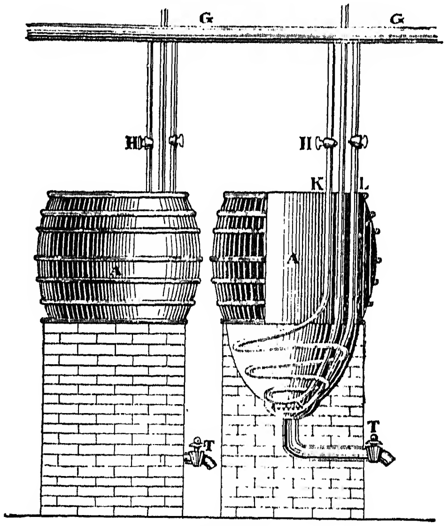

FIG. 303A.

$NaOH$, but practically rather more than this amount is used. *Tallow soap* is made in the following manner: The tallow is mixed and gently heated in the copper with about one-fourth of the necessary amount of caustic soda in the form of a solution of 10° Bé. First of all an emulsion is formed and then saponification gradually proceeds, the mass begins to become homogeneous and to boil gently and the volume to increase slightly. When a little is removed on the blade, it forms a jelly which does not separate the lye, and the soap-boiler judges of the fixation of the alkali by observing when the caustic taste of the alkali disappears. Much of the fat remains unsaponified, so that a hot caustic soda solution

of 12° to 14° Bé. is gradually added until the stirred, boiling mass thickens, becomes clear and homogeneous, and falls from the spatula in transparent ribbons. At this stage, in order to judge if the alkali has been added in the proper proportion, a little of the soap is poured on to a glass plate ; if a solid white edge first forms round the drop of soap, while the interior of the mass remains transparent until solidification is almost complete, the whole of the fat is saponified and there is no excess of alkali. If, however, the edge immediately turns greyish and the mass turbid, non-saponified fat is present and alkali lacking, whereas, if the whole mass becomes covered with a whitish pellicle without previous formation of a solid edge, excess of alkali is present, this being corrected by adding a little fused tallow to the mass in the copper. Thus treated, the gluey paste, which has a slightly caustic taste, is boiled more strongly until it loses sufficient water to form a homogeneous ropy paste on the mixing-blade.

At this stage the separation of the soap from the liquid is induced by the gradual addition of salt either in the solid state (4 to 8 per cent. of the weight of fat) or in concentrated solution (20° to 22° Bé.). The first addition of salt renders the mass more fluid, while successive additions cause separation of the soap, which finally floats on the lye, the latter being drawn off after some hours by means of either a tap or a siphon. When hard water is used, a little sodium carbonate is always added to the salt.

The residual lye should have not a caustic, but a brackish and somewhat sweet taste owing to the glycerine present, and its density should be at least 7° to 8° Bé. (for soaps from coconut, palm-kernel, oxidised oils, etc., 16° to 24° Bé.). If too little salt has been added, the lye will retain dissolved soap, and the separation of the latter will not be sharp, since between it and the lye will be formed a third layer consisting of an irregular, gelatinous mass which increases the waste and diminishes the yield. With too much salt, the soapy mass separates rapidly and in large clots which retain the lye, but if the operation has been properly carried out, the soap adheres to the mixer in soft flocculent masses which, when squeezed between the fingers, are moderately stiff, do not exude liquid and give a hard and dry, not a sticky, flake.

When treated repeatedly with salt solution, some soaps lose part of their combined alkali owing to the readiness with which they dissociate ; in such cases a little caustic soda is added to the salt.

The soap is then subjected to the *boiling* process (in some cases this is preceded by a further heating with weak alkali of 4° to 6° Bé. and a little salt, the subnatant lye being decanted after a time). This consists in covering the copper, boiling vigorously, and, if necessary, stirring to prevent the frothing mass from overflowing. By this means the small quantity of residual lye is concentrated and hence separates more easily, while the soap gradually becomes denser owing to the loss of nearly the whole of the water (only 15 to 35 per cent. being left). The bubbles at the surface gradually increase in size and then disappear completely, while large bubbles of steam form at the bottom of the copper, force their way noisily through the mass and produce large puffs at the surface. The heat (fire or steam) is then very soon stopped. A little of the soap pressed between the thumb and the palm of the hand then forms a dry, soft, waxy paste, but does not stick.

The soap could next be moulded, but it is often subjected to a *finishing* process (*see above*), dilute caustic soda (3° to 6° Bé., or hot water alone if the soap has been treated originally with excess of alkali, or very dilute sodium carbonate) being gradually added to the soap in the boiler, the mass being heated and gently stirred until it becomes more liquid, less granular and perfectly uniform. The copper is next covered and left for a day, the soap being then transferred to the moulds or cooling frames. To obtain white soap, an addition of 0·2 to 0·3 per cent. of sodium hydrosulphite is sometimes made to the mass before discharging.

As a rule, soaps are made not from pure tallow, but from mixtures of various fats and oils, *e.g.*, palm oil, olive oil, oleine, etc. ; in such cases the concentration of the caustic soda must be varied, olive oil soap, for example, requiring lye of 25° to 28° Bé., which sometimes renders salting-out unnecessary.

At one time *Marseilles soaps* were prepared from olive oil alone, very dilute lye being first used and then more and more concentrated ones, but nowadays cottonseed, arachis, coconut, palm-kernel oils, etc., are generally added, the processes employed, whether for white or for Marseilles mottled soap, being those used for other soaps.

SOAPS FROM FATTY ACIDS or OLEINE. Oleine, elaine, or commercial oleic acid forms a more or less dense liquid with a colour varying from pale yellow to dark brown.

Less highly coloured is the oleine obtained by saponification of pure fats in autoclaves and separation from the stearine by pressing (*oleine of saponification*) or by enzymic or catalytic decomposition (*catalytic oleine*), whilst that obtained from impure fats (bone fat, etc.) or by means of sulphuric acid is generally darker and is separated after distillation of the fatty acids (*distillation oleine*). If an oleine contains more than 3 per cent. of non-saponifiable substances, it is certainly distillation oleine (1 to 9 per cent.), but a less content than this does not necessarily indicate oleine of saponification since the modern methods of exact distillation yield oleines almost free from non-saponifiable matter.

Oleine always contains small quantities of neutral fats and, more especially, of solid fatty acids (5 to 20 per cent. palmitic, stearic, etc.), but its iodine number should be between 75 and 85, and its acid number at least 179 (about 90 per cent. of fatty acids, expressed as oleic acid).

Saponification oleine was at one time sold at a rather lower price than tallow, and distillation oleine at a still lower price (before the War at £24 to £28 per ton). Besides for soap-making it is used for treating wool which is to be carded or combed.

Pure oleic acid and its properties have already been considered on p. 358.

The manufacture of soap from fatty acids (*see* pp. 505 *et seq.*), although it gives no glycerine, is economical in various ways; thus, it allows of a more rapid saponification with a diminished consumption of fuel and renders possible the use of sodium carbonate which is cheaper than caustic soda.

100 kilos of oleine would require about 19 kilos of sodium carbonate (instead of 13·5 of caustic soda), but in practice only about 90 per cent. of this amount is used, the saponification being completed with caustic soda in order to transform the small amount of neutral fat present in the commercial oleine. A hot solution (about 30 per cent.) of the whole of the sodium carbonate is prepared in a wide, shallow copper, the oleine being then added gradually in a thin stream, the mass being mixed and heated by a jet of direct steam so as to liberate the carbon dioxide and prevent the froth from overflowing; the latter end is best attained either by adding a little salt to the soda solution at the beginning or by the passage of a current of air. The caustic soda solution (15° to 18° Bé.) is then introduced and the whole heated, salted out and boiled, as already described for tallow soap. Pure oleine soap is at first rather soft, but it gradually dries, hardens, and becomes of a paler yellowish-brown colour than the fresh soap.

When soap is made from oleine and fats together, the latter are first saponified and the oleine added subsequently.

RESIN SOAPS are now made in large quantities and by almost all soap manufacturers. **Colophony** (*see* Part III) contains acids which behave like the fatty acids and yield similar soaps, which lather well with water and, when mixed with ordinary fat soaps, diminish the price considerably, as colophony costs only £7 to £14 per ton.

The saponification of the resin is effected with a rather strong lye (to avoid excessive frothing). It is necessary to employ pure fats and pure resin (with the saponification number 160 to 180), and when saponification is complete, the soap must be well "finished" in order to avoid excess of alkali, which would cause *efflorescence* (also avoidable by the addition of a little sodium silicate at the end of the manufacture).

The resin may be introduced as a powder directly into the fused fat, but it is more generally added after the fats have been saponified and the soap salted out and separated from the lye. The concentrated caustic soda (100 kilos at 20° Bé. or 90 kilos at 25° Bé. per 100 kilos of resin) is then added and the resin gradually disintegrated by heating and stirring. Boiling is continued until the froth almost disappears and the soapy mass separates well from the lye below and exhibits the proper consistency when pressed between the fingers. After the lye has been removed, the soap is finished with a little boiling water, then left for 12 to 24 hours, and finally solidified in the ordinary frames or moulds.

Good resin soaps should not contain more than 40 per cent. of resin, but in some cases they show as much as 100 per cent. (compared with the fat), and it is a question whether resin soap should be regarded as adulterated; to this view the manufacturers object for obvious reasons. Although attempts have been made at various congresses to fix limits (10, 20, or 30 per cent.) to the proportion of resin allowable, none of these are regarded. The case would be met by stamping the resin-content on every cake of soap, as there could then be no question of adulteration or fraud.

Some soaps are not separated from the lye, or grained or finished, but are left mixed with the lye and the glycerine; the fats employed must here be pure, since otherwise

the impurities would colour the soap. Coconut oil and palm-kernel oil are more especially used, as they have the property of becoming incorporated or remaining dissolved in a large excess of alkali or salt and of forming hard soaps with even large proportions of water (200 to 300 per cent.). They are made by either the hot or the cold process, and are generally cheap soaps, as they can be resined and charged, not only with large quantities of water, but also with salt, silicate, talc, flour, etc. Solutions of salt or caustic soda (20° Bé.), even in excess, facilitate hardening, whilst potassium carbonate produces a certain softness and lustre. The silicate and salt are mixed with hot caustic soda and are added finally to the soap at 90° to 95°. The method of procedure is that generally employed: the fat is added to part of the caustic or carbonate solution, with which it is stirred and heated to boiling; the rest of the alkali is then introduced and finally the salt or silicate solution in small portions; the mass is mixed, left in the covered copper overnight, when it falls to a temperature of 75°, then skimmed and cooled in the frames.[1]

When these soaps are prepared in the cold, the palm-kernel or coconut oil is mixed with the theoretical quantity of concentrated caustic lye (for coconut oil, 50 per cent. of lye at 38° Bé.), which saponifies these and other fats (tallow, lard, cottonseed oil, arachis oil, resin, etc.), even in the cold, with spontaneous rise of temperature; they are commonly loaded with silicate, talc, salt, etc.

MOTTLED SOAPS. Until 30 to 40 years ago, mottled soap of the Marseilles type was made with olive oil, the mottling being produced by adding to the soap, either before or after graining, ferrous sulphate, ferric oxide, ultramarine, etc. (0·2 to 0·6 per cent. of the weight of fat), discharging into the cooling frames at a temperature of 75° to 80° and allowing to cool slowly (four to six days).

Mottling is satisfactory only when the soap does not contain more than 32·5 to 34 per cent. of water, and hence constitutes a safeguard to the consumer, showing that he is not being cheated with soap overcharged with water. Olive oil soap can be well mottled if it does not contain more than the above quantities of water and colouring-matter, and not more than 2 per cent. of salt, since it is only under these conditions that it acquires just that fluidity which, at the solidifying temperature, offers a resistance to the minute coloured particles (iron, aluminium, and manganese soaps, and metallic hydroxides); the latter gradually group themselves into veins, whilst the drops of lye and soluble salts fall to the bottom. If the quantity of water is raised, the equilibrium is displaced and the fluidity increased, so that the colouring-matters are deposited, but if other solid fats are used in conjunction with the olive oil, the required consistency can be obtained with as much as 50 per cent. of water. With coconut, palm-kernel, and palm oils, mottled soaps can be prepared containing 70 per cent. or even more of water, in addition to an increased amount of alkali. These soaps, however, should not contain more than 2 per cent. of sodium carbonate, and less than 10 per cent. of dissolved salts; otherwise the soap will effloresce on drying, provided that it is sufficiently stiff to permit of mottling.

A type of mottled soap which is often prepared with a yield of 180 to 200 per cent. is that from almost equal quantities of sulphocarbon olive oil and coconut or palm oil. In this case the manufacture of the olive oil soap is carried out separately as far as the stage where it is separated from the lye, so as to remove the impurities; it is then introduced into the pan where the coconut oil has been saponified in the hot with caustic soda of about 20° Bé., together with some 13 per cent. of sodium carbonate dissolved in water. Unger (1869) found that, in order to prevent coconut or palm oil soap from efflorescing on drying, it should not contain more than 43 per cent. of sodium carbonate, calculated on

[1] High yields are given by the following mixtures:—

Yield	Coconut oil	Crude palm-kernel oil	Palm oil	Tallow	Resin	Caustic soda (26° Bé.)	Potassium carbonate 25°–30° Bé.	Salt		Sodium Silicate
								20°–22° Bé.	8°–10° Bé.	
	kilos	kilos								
About 250 %	90	[or 90]	—	10	—	60	65	40	—	—
,, 300 %	—	100	—	—	—	60	100	65	—	—
,, 300 % (resined)	50	40	20	—	15	60	65	65	—	—
,, 400 %	100	[or 100]	—	—	—	60	100	100	50	30
,, 800 %	100	[or 100]	—	—	—	80	260 (20° Bé.)	300	60	—
,, 1000 %	100	—	—	—	—	150–160 (22° Bé.)	—	—	—	800

the weight of coconut oil (*i.e.*, 1 mol. of sodium carbonate per 4 mols. of pure coconut soap). After mixing, the two soaps are boiled and 4 to 5 per cent. (on the total fat) of sodium chloride solution of 24° Bé. gradually added; the heating is continued until the paste boils readily without adhering to the sides of the copper, and the steam evolved produces, at the surface of the soap, veinings and crevices in the form of rosettes. The soap will then emit a hollow sound and will not form bubbles when struck with the stirrer, from which it falls in broad folds which become covered with a dry skin, while between the fingers it does not pull out, but tends to solidify. It is important that it should not contain an excess of caustic soda (not more than 0·2 to 0·3 per cent.; it is *best neutral*) as with finished soaps; any excess may be eliminated by adding the calculated quantity of coconut oil or of hydrochloric acid, determined by titration. At this point the colouring matter is well mixed in, the soap being then cooled to about 75° and poured into large solidifying frames (holding at least a ton) so as to cause slow cooling (in winter these are wrapped round with cloths), and hence satisfactory mottling. These mottled soaps of high yield (up to 400 per cent.) bear the name of blue mottled or *Eschweg soaps*, and were largely used some years ago. Even now their consumption is considerable, as they have a higher detergent power than finished soaps owing to their richness in alkali carbonates; they dry more rapidly than resin soaps and owing to their hardness they are preferred for laundry purposes, there being no waste even when the clothes are vigorously rubbed.

The formation of mottling in soaps probably obeys the laws holding in the solidification of alloys (*solid solutions*) and the figures given on pp. 515 and 810, and in Plates I. and

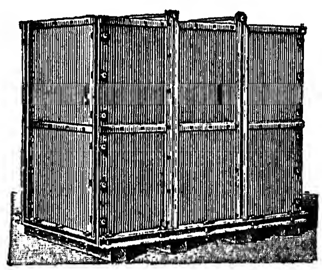

FIG. 304.

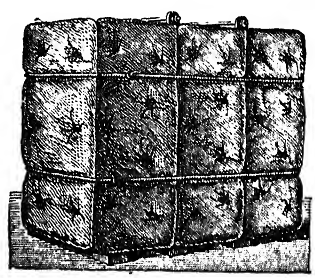

FIG. 305.

II., p. 830, of Vol. I. of this work ("Inorganic Chemistry") represent well the impression produced by the mottling of soap.

When *almond-mottling* is required, an iron rod 12 to 15 mm. in diameter is drawn vertically through the semi-solid soap in the solidifying frame, so as to make a kind of longitudinal cut; similar cuts, parallel to the first, are then made throughout the whole mass at distances of 4 to 6 cm., and afterwards a similar series perpendicular to the others. When solidification is complete, the whole of the soap is traversed by dark markings in the shape of almonds arranged like the leaves on acacia twigs. Other mottlings are made either by machinery or by hand.

For Eschweg soaps mixtures of various fats are used, *e.g.*, 20 to 25 per cent. of tallow, 25 to 30 per cent. of bone fat, 10 to 15 per cent. of cottonseed oil, 20 to 40 per cent. of palm-kernel oil, and 20 to 30 per cent. of coconut oil. The yield is usually 205 to 215 per cent., although additions of silicate (10 to 12 per cent.) are sometimes made.

TRANSPARENT SOAPS were at one time obtained by dissolving ordinary soaps in alcohol, evaporating the latter and moulding the transparent residue. The amount of alcohol used was subsequently diminished by adding glycerine, and at the present time transparent or so-called glycerine soaps are made from mixtures of decolorised tallow with castor, linseed, and coconut oils, with addition of glycerine and also of 20 to 30 per cent. of saccharose or glucose, which enhances the transparency. To this mixture, melted in the copper, is added caustic lye at 30° to 36° Bé., the whole being mixed until a homogeneous emulsion is formed; 2 to 5 per cent. of alcohol is then introduced, and the mass heated to 75°, cooled to 50°, and poured into the moulds. For some of these soaps as much as 40 per cent. of pale resin is employed.

SOFT SOAPS are usually potash soaps of linseed oil or oleine, while in summer cottonseed, colza, sesamé, palm, or fish oil is also used.

Some of these soaps are transparent (plain or variegated), others opaque and white or yellowish. For every 100 kilos of fat, about 160 kilos of caustic potash of 24° Bé. are used, the yield being sometimes as much as 235 per cent. ; if caustic soda is partly employed, a harder soap is obtained, but the yield is diminished. Also 10 to 15 per cent. of resin may be used or 10 to 15 per cent. of oil. In general these soaps contain carbonates.

The boiling is carried out in the usual way, and is continued until frothing ceases, and

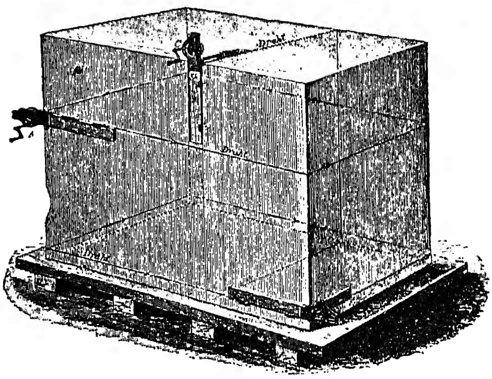

Fig. 306.

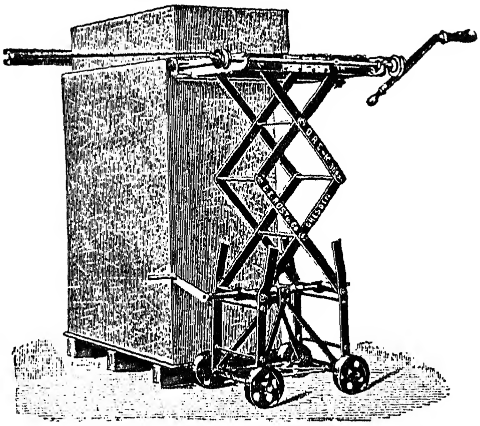

Fig. 307.

a small portion placed on glass remains clear for some time without forming a skin and, on cooling, becomes turbid at the edges and exhibits slight veinings of lye. If this test portion remains clear but presents no such veinings, lack of alkali is indicated.

Many of the soft soaps now used contain white granules, produced by the addition of tallow or stearine, which crystallises out throughout the mass of soap during the cooling, the latter occupying 4 to 8 weeks ; this change is known as *figging* and the yield of such soaps is often as high as 240 per cent.

The manufacture of soda soap from glycerides by means of lime and sodium carbonate (Krebitz process) has been described on p. 505.

Cooling and Solidification. The soap from the copper is cooled in large chests or *frames*, formerly of wood but now of iron, as was suggested by Krull in 1876 (Fig. 304). The sides of these are fixed by means of bolts and nuts and hence fit perfectly and are readily taken apart. In some cases, the frames are mounted on three wheels so as to be transportable. To prevent any impurities depositing in one place and so producing mottling, the pasty soap in the frame is stirred with wooden *crutches* until it begins to solidify, but if slow solidification is required (for mottled soaps), the sides of the frame are covered with straw mattresses or wool, especially in winter (Fig. 305). The frames vary in capacity from 100 to 6000 kilos and, according to the amount and quality of the soap, the cooling lasts one or several weeks. The walls of the frame are then removed and the large block cut into smaller prismatic blocks by means of thin steel wires worked by a toothed-wheel winch, which is applied to various points of the block (Fig. 306). The small blocks are discharged on to a truck carrying a platform which can be raised (Fig. 307) and are then transferred to the *barring machine* (Fig. 308), where each block is placed between *A* and *B*

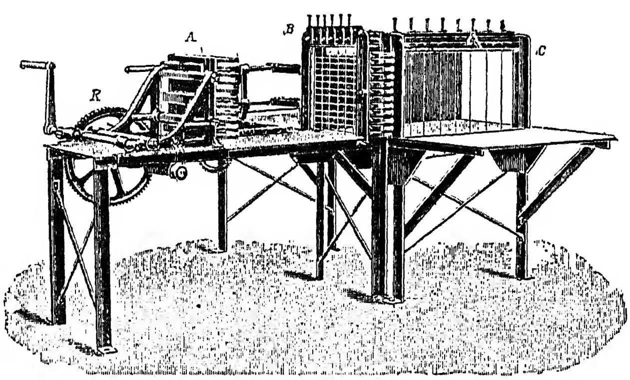

Fig. 308.

and forced by means of the plate *A* and the toothed wheel, *R*, against the frame, *B*, fitted with adjustable crossed steel wires. The long bars thus obtained between *B* and *C* are then pressed against the vertical wires of the frame, *C*, and thus cut into cakes of the required size. There are many such machines of different types, some fitted with fixed and others with universal frames.

During recent years a method has been devised of preparing cakes directly from the hot soap from the copper, without using the large cutting machines (*slabbers*); in this way much time is saved, waste and scraps are diminished in amount and the subsequent seasoning shortened. The hot soap is rapidly cooled and compressed in the Klumpp apparatus (Fig. 309), being first transferred to the jacketed reservoir, *L*, where it is kept liquid by means of hot water in the jacket. The plate, *c*, consisting of a double-walled box surrounded by cold water, has a movable base, *h*, resting on the piston of a hydraulic pump, *K*. The box, *c*, is filled with liquid soap and the wheel, *V*, turned so as to press on to the surface of the soap the large plate, *a*, which is kept horizontal by the four rods, *N*, of the press, while inside it cold water circulates.

When this plate is firmly fixed and the soap begins to solidify, a pressure of 50 atmos. is applied by means of the press, *K*, this pressure being increased to 250 atmos. when the soap is quite cold and solid. The ordinary cutting machines are then used to cut these slabs into marketable pieces, which lose little water even in the air.

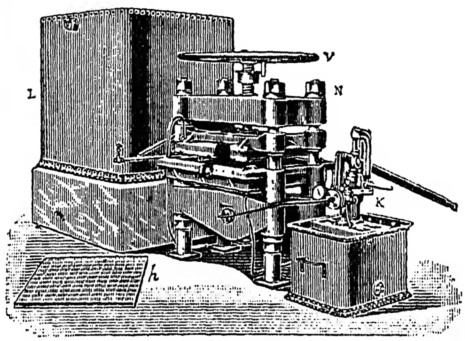

FIG. 309.

Seasoning or *drying* of the soap, to bring it to the degree of moistness required by the trade, is effected by keeping the cakes on frames in well-ventilated chambers for several weeks or even months. This slow drying is now generally replaced by drying in hot air, furnished cheaply by Perret furnaces, which burn waste coal or slack. The soap is spread on gratings superposed on trucks, which are gradually introduced into a brickwork gallery; hot air traverses the gallery, entering at the opposite end at 50° to 60° and being discharged at 35° to 45°. The seasoning is complete in 3 to 6 days, but if the temperature is too high at first, or the drying too rapid, the soap softens and becomes deformed and crushed. To give the cakes a smooth surface, and so render efflorescence and cracking more difficult, as they issue from the dryer they are subjected to the action of a slight steam-jet, which melts them superficially.

The value of soap [1] varies considerably with the quality, the degree of fineness, the

[1] **Analysis of Soap.** As a rule, the commercial value of a soap is determined from the quantity of combined fatty acids which it contains, and as the percentage of these varies with the degree of moistness, great care must be taken in sampling the soap. The cake is first weighed and the sample cut in such a way that the inner and outer portions are taken in the proper proportions; the sample is then cut up fine, rapidly mixed and immediately enclosed in a vessel with a ground stopper so that water may not be lost.

The analysis consists of some or all of the following determinations:

(1) *Water.* This estimation is not usually made, as it involves a long operation, while it is possible to calculate the proportion of water indirectly after all the other components have been determined. The direct estimation is made by weighing 5 to 10 grms. of the finely divided soap rapidly in a tared dish containing a small glass rod and filled to the extent of one-third with sand which has been previously calcined. The dish and its contents are heated first in an oven at 60° to 70°, the fused soap being carefully mixed with the sand until a skin of soap no longer forms at the surface; the temperature is then raised to 105° to 110°, at which it is maintained until constant weight is reached. The total loss in weight represents the water.

(2) *Unsaponified Fat.* The *dry* residue from the water estimation is introduced into a Soxhlet extractor (*see* p. 462) and extracted for a couple of hours on the water-bath with light petroleum in a tared flask; the solvent is subsequently distilled off and the extracted fat dried at 110° until of constant weight.

(3) *Fatty Acids, Free Alkali, Glycerine, and Resin.* The residual matter in the Soxhlet apparatus (or the dry soap itself) is extracted with neutralised absolute alcohol, which dissolves the soap, glycerine, and *free caustic alkali:* the last of these is determined immediately by titrating the alcoholic solution with normal sulphuric acid in presence of phenolphthalein. The liquid is afterwards largely diluted with water, heated for a long time on the water-bath to remove all

content of fatty acids, and the degree of purity. The ordinary soaps used in laundries and in the textile industries, which are made from sulphocarbon olive oil and contain 60 to 65 per cent. of fatty acids, cost before the war £22 to £24 per ton, according to the conditions of the market and the prices of prime materials (fats and oils). Soaps loaded with water and other substances may cost much less ; fine, perfumed soaps cost up to £40 to £80 per ton.

GG. POLYHYDRIC ALDEHYDIC OR KETONIC ALCOHOLS

CARBOHYDRATES

(Sugars, Starch, Cellulose)

This group of substances might have been included in the preceding chapter, **FF**, where, in paragraphs **D** and **E**, certain very simple aldehydic and ketonic alcohols have been considered. Partly owing to custom [since it has been the rule to include in the group of **Carbohydrates** only ketonic or aldehydic polyhydric alcohols with six (*monosaccharides*) or a multiple of six carbon atoms (*polysaccharides*) and containing hydrogen and oxygen in the proportion of 2 : 1, as in water], and partly because this group embraces all the sugars, which exhibit special characters very different from those of glycollic aldehyde (which should be the first member), the carbohydrates are, however, considered separately, although the brilliant researches of Emil Fischer, commenced in 1887, have extended this group to compounds with five, four, or three carbon atoms, on the one hand, and to monosaccharides with six, eight, or even nine carbon atoms on the other.

These monosaccharides bear the name of **Monoses** (*bioses*, *trioses*, *tetroses*, *pentoses*, *hexoses*, *heptoses*, *octoses*, *nonoses*, etc., according to the number of carbon atoms they contain), while the polysaccharides (formed by the condensation of two or more monose molecules) are called generally *polyoses* and,

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the alcohol, and treated with a measured volume, in excess, of normal sulphuric acid, the liquid being then heated in a beaker on a water-bath and on a sand-bath until the *clear* fatty acids (and the resin, if present) separate at the surface. After cooling, the solidified layer of acids is pierced with a rod and the liquid poured on to a tared filter in a stemless funnel, the fatty acids being then washed with hot water, and the whole brought on to the filter. The excess of free sulphuric acid in the whole of the wash-water is determined by titration with normal caustic potash. This then gives the amount of sulphuric acid fixed by the alkali of the soap and hence also the *combined alkali* expressed as Na_2O. Evaporation of the liquid to dryness and extraction with absolute alcohol removes any *glycerine* present in the soap, this being weighed after evaporation of the alcohol. The fatty acids on the filter are treated with a couple of c.c. of alcohol to remove any moisture and then with sufficient light petroleum to dissolve all these acids; the filtrate is evaporated in a tared dish, dried at 105° to constant weight and the residual *fatty acids* weighed. To determine any *resin* which may be present in the fatty acids, part of the latter is weighed, dissolved in 20 c.c. of alcohol and, after addition of phenolphthalein, hydrolysed in the hot with a slight excess of alkali; after cooling, the liquid is made up to 110 c.c. with ether, treated with powdered silver nitrate and allowed to deposit the precipitated silver stearate, palmitate, and oleate. One-half of the filtered solution (containing soluble silver resinate) is treated with 20 c.c. of dilute hydrochloric acid (1 : 2) and filtered, an aliquot part of the filtrate being evaporated in a tared capsule, dried at 100° and the residual *resin* weighed ; the weight of the resin is diminished by 0·00235 grm. for every 10 c.c. of ethereal solution of silver resinate, this being the amount of oleic acid removed by the ether. The true weight of the fatty acids, free from resin, can then be calculated.

(4) *Soda, Salt, Sulphates, Silicate, etc.* The residue from the Soxhlet apparatus, after separation of the fat and soap, is treated two or three times with 50 to 60 c.c. of hot water and the solution filtered, made up to a definite volume and divided into four parts: one of these is titrated with normal sulphuric acid, using phenolphthalein as indicator, to ascertain the *sodium carbonate :* in a second portion, the *sodium chloride* is determined by titration with silver nitrate; the third is precipitated with barium chloride and the weight of the barium sulphate and hence that of the *sodium sulphate* in the soap, determined. The fourth portion is treated with hydrochloric acid and the silica, thus separated from the silicate, weighed.

(5) *Ash and Mineral "Filling."* The ash obtained by burning a definite weight of pure soap is about 40 per cent. greater than the total alkali (expressed as Na_2O). If the proportion is much higher than is indicated by this relation, the excess represents mineral *filling*.

in particular, hexabioses, hexatrioses, etc., according as they are formed by the condensation of two, three, etc., hexose molecules.

A. MONOSES

All the monoses are aldehydic or ketonic polyhydric alcohols containing the characteristic grouping, $\begin{array}{c}\mathrm{H}\\ -\mathrm{C}-\mathrm{C}-\\ \mathrm{OH}\ \ \mathrm{O}\end{array}$, *i.e.*, a hydroxyl group united with a carbon atom adjacent to a carbonyl (CO) group. When the carbonyl exists as an aldehydic group, $\begin{array}{c}\mathrm{H}\\ -\mathrm{C}-\mathrm{C}\cdot\mathrm{H}\\ \mathrm{OH}\ \ \mathrm{O}\end{array}$, these monoses are called **Aldoses**, whilst when it exists as a ketonic group, $\begin{array}{c}\mathrm{H}\qquad\ \ |\\ -\mathrm{C}-\mathrm{C}-\mathrm{C}-\\ \mathrm{OH}\ \ \mathrm{O}\quad\ |\end{array}$, they are termed *ketoses*, so that we have *aldohexoses*, *ketohexoses*, etc.[1]

The monoses have the general properties of the aldehydes or ketones and hence form, on oxidation, the corresponding monobasic acids, *e.g. pentonic, hexonic acids,* etc. Since the aldoses contain a primary alcoholic group,

$$OH \cdot CH_2 \cdot [CH \cdot OH]_n \cdot C\begin{array}{l}\nearrow O\\ \searrow H\end{array},$$

they can also be oxidised to dibasic acids, containing the same number of carbon atoms, whilst when the ketoses are oxidised, the carbon atom chain is ruptured and acids with lower numbers of carbon atoms formed.

On reduction, both the aldoses and the ketoses take up two atoms of hydrogen, forming the corresponding alcohols; the hexoses give *hexitols* and the pentoses *pentitols.*

Like all aldehydes, they reduce ammoniacal silver solutions in the hot, giving silver mirrors.

When heated with alkali, they turn brown and then resinify.

They reduce alkaline copper solution (Fehling's solution) in the hot (*see* p. 255, *and later*).

When heated with excess of phenylhydrazine dissolved in acetic acid, they yield yellow, crystalline *phenylosazones*, insoluble in water.[2]

[1] The two classes of sugars, *aldoses* and *ketoses*, are distinguished by means of Romijn's reaction with a solution of iodine and borax, which *oxidises all the aldoses* (galactose, glucose, mannose, arabinose, xylose, rhamnose, maltose, lactose), while it either does not oxidise the *ketoses* or oxidises them but slightly (sorbose, fructose; saccharose and raffinose are oxidised to a small extent). Betti (1913) finds that the aldoses, but not the ketoses, react with β-naphtholbenzylamine, forming crystalline products.

[2] They form first *phenylhydrazones* (*see* p. 246):

$$\begin{array}{l}\quad\ \ |\\ \mathrm{H{-}C{-}OH}\\ \quad\ \ |\\ \quad\ \ \mathrm{C} = \boxed{\mathrm{O} + \mathrm{H_2}}\mathrm{N{\cdot}NH{\cdot}C_6H_5}\\ \quad\ \ |\end{array} = H_2O + \begin{array}{l}\quad\ \ |\\ \mathrm{H{-}C{-}OH}\\ \quad\ \ |\\ \quad\ \ \mathrm{C} = \mathrm{N{\cdot}NH{\cdot}C_6H_5}\\ \quad\ \ |\end{array};$$

these *phenylhydrazones* then react with two other molecules of phenylhydrazine, giving ammonia, aniline, and *phenylosazone :*

$$\begin{array}{l}\quad\ \ |\\ \mathrm{H{-}C{-}O{-}H} \qquad \mathrm{NH_2\,NHC_6H_5}\\ \quad\ \ | \qquad\qquad\quad + \mathrm{H_2\,N{\cdot}NHC_6H_5}\\ \quad\ \ \mathrm{C{=}N\,NH{\cdot}C_6H_5}\\ \quad\ \ |\end{array} = \underset{\text{aniline}}{NH_3 + NH_2{\cdot}C_6H_5} + H_2O + \begin{array}{l}|\\ \mathrm{C{=}N{\cdot}NHC_6H_5}\\ |\\ \mathrm{C{=}N{\cdot}NHC_6H_5}\\ |\end{array}$$

In dealing with the hexoses later, we shall see how the constitutions of the monoses in general are determined.

Of the various monoses, containing from 2 to 9 carbon atoms, only certain of the hexoses are *fermentable*, that is, give alcohol and carbon dioxide under the action of ferments or enzymes (*see* pp. 134 and 146). Of the hexoses, some ferment readily, others with difficulty, and others again not at all, in dependence on their stereochemical configurations and possibly on the asymmetric constitution of the enzymes. d-Glucose, d-mannose, and d-fructose ferment easily, and d-galactose with difficulty, whilst l-glucose and l-mannose do not ferment.

GENERAL METHODS OF FORMATION OF THE MONOSES :

(*a*) From the polyoses by *hydrolysis* with dilute acids, water being added and several molecules of hexose obtained :

$$C_{12}H_{22}O_{11}\ (\text{saccharose}) + H_2O = 2C_6H_{12}O_6.$$

(*b*) By oxidation of the corresponding alcohols by nitric acid : *e.g.*, **Arabitol**, $C_5H_{12}O_5$, gives **Arabinose**, $C_5H_{10}O_5$ (pentose) ; *xylitol* (stereoisomeric with arabitol) gives xylose, and **Mannitol**, $C_6H_{14}O_6$, mannose.

(*c*) Oxidation of glycerol gives dihydroxyacetone, $OH \cdot CH_2 \cdot CO \cdot CH_2 \cdot OH$, which is a triose, its constitution being indicated by the fact that it forms a cyanohydrin, $OH \cdot CH_2 \cdot C(OH)(CN) \cdot CH_2 \cdot OH$, the latter yielding *trihydroxyisobutyric acid*, $OH \cdot CH_2 \cdot C(OH)(COOH) \cdot CH_2 \cdot OH$, and this, on reduction, isobutyric acid having a known constitution.

(*d*) By treating the bromo-derivatives of the aldehydes with baryta water. Thus monobromaldehyde gives **Glycollic Aldehyde**,

$$CH_2Br \cdot C\left\langle\begin{matrix}O\\H\end{matrix}\right. + H_2O = HBr + OH \cdot CH_2 \cdot C\left\langle\begin{matrix}O\\H\end{matrix}\right. ,$$

which is the *simplest member of the sugar group* and does not gives all the reactions of the sugars.

(*e*) With lime-water, formaldehyde undergoes *aldol condensation* (*see* p. 245), giving **Formose**,

$$6\ H \cdot C\left\langle\begin{matrix}O\\H\end{matrix}\right. = OH \cdot CH_2 \cdot CH(OH) \cdot CH(OH) \cdot CH(OH) \cdot CH(OH) \cdot C\left\langle\begin{matrix}O\\H\end{matrix}\right. ,$$

which is a syrupy mixture of compounds, $C_6H_{12}O_6$.

Under the influence of light and moisture, plants fix CO_2 and form starch $(C_6H_{10}O_5)_n$, which is a polyhexose, $6CO_2 + 6H_2O = C_6H_{12}O_6 + 6O_2$, the hexose then giving up water and yielding starch. According to Baeyer (1870), the CO_2 gives first formaldehyde, then a hexose (monose), and finally starch (polyose).[1]

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which is the characteristic group of the phenylosazones. The latter crystallise readily and in a pure state from a dilute pyridine solution. Reduction of the phenylosazones yields *osamines*, *e.g.*, *glucosamine*, $C_6H_{11}O_5 \cdot NH_2$.

[1] From the analogy in the behaviour of hæmoglobin and chlorophyll, Baeyer supposed the latter, like the former, to be capable of uniting with carbon monoxide. In such case the chlorophyll would decompose CO_2 into O and CO, and water into O and H_2, the oxygen being evolved ; the CO, fixed by the chlorophyll, would split off and combine with the hydrogen to give formaldehyde, the chlorophyll being regenerated. Union of the formaldehyde with H_2O would then yield methyleneglycol, $CH_2(OH)_2$, which would condense to glucose: $6CH_2(OH)_2 = 6H_2O + C_6H_{12}O_6$. Baeyer's hypothesis does not seem satisfactory, since dissociation of two highly exothermic substances like CO_2 and H_2O is difficult to conceive, while, in addition, plants are indifferent towards CO.

It was shown by Butlerow that formaldehyde—and later by E. Fischer that glyceraldehyde—can, under certain conditions and in the presence of bases (baryta), give rise to sugar (*α*-acrose). In 1905 H. and A. Euler found that under no conditions do other alkali hydroxides give an appreciable amount of sugar, whilst with dilute solutions of sodium carbonate or, better, with calcium carbonate or lead hydroxide at 100°, first glycollaldehyde and glyceraldehyde are formed and finally a *keto-arabinose*, the phenylosazone of which melts at 159° to 161°. The conditions for the production of hexoses from formaldehyde are not yet defined, but O. Loew stated that, with milk of lime, he obtained *formose*, which is a mixture containing *i-fructose* (*α-acrose*).

D. Berthelot and H. Gaudechon (1910) found that the action of ultra-violet rays on 10 per

Also 2 mols. of glyceraldehyde (derived, *e.g.*, from acroleïn) undergo the aldol condensation and yield a hexose (termed *acrose*) which is a constituent of formose.

(*f*) It is possible to pass from one aldose to a higher one through the cyanohydrin, which is first hydrolysed to an acid with an extra carbon atom. Such an acid readily forms a *lactone* with the hydroxyl in the γ-position, and treatment of the lactone with sodium amalgam (addition of H_2) yields the higher aldehyde (aldose):

$$OH \cdot CH_2 \cdot CH(OH) \cdot CH(OH) \cdot CH(OH) \cdot CH(OH) \cdot C\Big\langle{}^{O}_{H} \rightarrow$$

$$\overset{1}{OH \cdot CH_2} \cdot \overset{2}{CH(OH)} \cdot \overset{3}{CH(OH)} \cdot \underset{\gamma}{\overset{4}{CH(OH)}} \cdot \underset{\beta}{\overset{5}{CH(OH)}} \cdot \underset{\alpha}{\overset{6}{CH(OH)}} \cdot \overset{7}{COOH} \rightarrow$$

$$OH \cdot CH_2 \cdot CH(OH) \cdot CH(OH) \cdot \overset{\gamma}{CH} \cdot CH(OH) \cdot CH(OH) \cdot CO + H_4 \rightarrow$$
$$\underbrace{\qquad\qquad\qquad\qquad\qquad}_{O}$$

$$OH \cdot CH_2 \cdot CH(OH) \cdot CH(OH) \cdot CH(OH) \cdot CH(OH) \cdot CH(OH) \cdot C\Big\langle{}^{O}_{H} .$$

Heptose.

By the same ketonic (lactonic) synthesis, the *heptose* can be converted into *octose* and *nonose*.

TETROSES, $C_4H_8O_4$, and PENTOSES, $C_5H_{10}O_5$

Just as the hexoses can be converted into pentoses, the latter can give rise to TETROSES. For instance, *d*-, *l*-, and *i-erythrose* are obtained by oxidising

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cent. solutions of various sugars at a temperature of 80° to 90° leads to the rapid formation of the following quantities of gas:

	CO	CH_4	H_2	CO_2
Levulose (ketose)	83	8	9	15
Glucose (aldose)	12	12	76	22
Maltose (gives 2 mols. glucose) . .	12	11	77	21
Saccharose (gives glucose and levulose) .	45	8	47	16

They found also that prolonged action of ultra-violet rays on a mixture of CO_2 and H_2 yields a small quantity of CO and of formaldehyde.

These facts tend to confirm J. Stoklasa's observations (1906–1910) on the formation of hydrogen as final product of the degradation of carbohydrates by the action of *glycolytic enzymes*, which have an important function in the assimilation of carbon dioxide in the chlorophyll cells, and also to render valid Stoklasa's hypothesis (1907) that the formaldehyde necessary to the formation of carbohydrates by the simple polymerisation assumed by Baeyer may result from the reaction, $2CO_2 + 2H_2 = O_2 + 2H{\cdot}CHO$. Stoklasa and Zdobnický (1910) have obtained inactive sugars and aldehyde by the action of ultra-violet rays on carbon dioxide and hydrogen in the nascent state in presence of caustic potash (with initial formation of potassium bicarbonate, which, in the nascent state and with nascent hydrogen, generates the sugar) and have disproved the view held by Fischer (1888–1889), Loew (1888–1889), Neuberg (1902), and Euler (1906) that, in the synthesis of sugars from formaldehyde, pentoses are formed; the sugars they obtained are not asymmetric and are hence not fermented by ordinary alcoholic ferments. In 1912 Stoklasa, Šebor and Zdobnický showed that formic acid constitutes an intermediate product in the formation of CO_2 and H_2O by the action of ultra-violet light on formaldehyde in presence of potassium hydroxide and air. Subjection of CO_2 and KOH, mixed with a ferrous salt, to the influence of ultra-violet rays gives hexoses (aldoses and ketoses) which are optically inactive and non-fermentable. According to Stoklasa, the function of the *chlorophyll* in plants is to absorb the ultra-violet rays of sunlight. From the aqueous distillate of the leaves of various plants, F. Hartwig and T. Curtius (1910) have separated (by means of m-nitrobenzhydrazide,

α : β-hexylenealdehyde, $CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH : CH{\cdot}C\Big\langle{}^{O}_{H}$, the hydrazone of which melts at 167°.

According to Baur (1913) the formation of carbohydrates in green plants from CO_2 is probably accompanied by the transitory formation of various acids and alcohols. Similarly the genesis of sugars in the animal organism may result from the glycine which forms a product of the decomposition of the proteins and produces glycollic acid and formaldehyde in passing through the liver.

Baly, Heilbron and Barker (1921) find that aqueous carbon dioxide solution yields formaldehyde when exposed to light of wave-length 200 $\mu\mu$, the yield of the aldehyde being greatly increased in presence of paraldehyde, sodium phenoxide and certain salts which absorb light of wave-length 290 $\mu\mu$; these substances protect the formaldehyde produced from the polymerisation to reducing sugars effected by this light (290 $\mu\mu$). Chlorophyll appears to be an ideal photo-catalyst for both stages of the synthesis of carbohydrate from carbon dioxide and water, the absence of free formaldehyde in the growing leaf being thus explained.

d-arabonic acid, d-arabinosoxime, and natural *i-erythritol* respectively with hydrogen peroxide :

$$OH \cdot CH_2 \cdot [CH \cdot OH]_3 \cdot COOH + O = H_2O + CO_2 + \underset{\text{Tetrose}}{OH \cdot CH_2 \cdot [CH \cdot OH]_2 \cdot CHO}$$

The tetroses are also obtained by oxidising (with H_2O_2) the calcium salts of pentonic acids in presence of ferric acetate, which acts as an oxidising catalyst.

The pentoses (**Arabinose, Xylose,** etc.) occur abundantly as **Pentapolyoses** or **Pentosans (Araban, Xylan)** in many vegetable organisms (straw, wood, maize husks, etc.), from which they are obtained by simple boiling with dilute acids.[1] So-called non-nitrogenous *extractives* present in abundance in plants and in foods consist especially of pentoses, hexoses, *lignin* and *cutin* (König, 1913), which exhibit varying solubility in water and in acids at different temperatures and pressures. Pentoses do not ferment.

Arabinose and xylose are aldoses, $OH \cdot CH_2 \cdot [CH(OH)]_3 \cdot CHO$. By bromine water these two pentoses are oxidised with formation respectively of *arabonic* and *xylonic acids*, $OH \cdot CH_2 \cdot [CH \cdot OH]_3 \cdot CO_2H$, which are stereoiso-

[1] By the term **Pentosans** are meant those polysaccharides which are related to the pentoses in the same way as are starch, inulin, etc., to the hexoses, and which give pentoses and also hexoses on hydrolysis. From starch they are distinguished by their lævo-rotation. From plants the pentosans are extracted by means of dilute alkali according to the method given by Tollens, Stone, and Schulze (1888–1901) : the finely divided vegetable matter is treated twice, for some hours at the ordinary temperature, with seven times its weight of 2 per cent. ammonia solution to eliminate in the soluble state part of the proteins, salts, etc., and to remove the more soluble part of the hemicellulose (this would give little pentose on subsequent hydrolysis). After the dark ammoniacal liquid has been separated by filtration through cloth and by squeezing in a press, the solid residue is extracted with ten times its weight of 5 per cent. caustic soda solution, with which it is first macerated in the cold for 10 to 12 hours, and then heated in a reflux apparatus on a water-bath for six hours. The mass is next filtered through cloth and the residue pressed and washed several times with water until the total volume of solution obtained is equal to that of the caustic soda solution used.

This brown liquid is evaporated to some extent on a water-bath and is then treated in the cold with an equal volume of 90 per cent. alcohol. The voluminous, flocculent precipitate of *gum* (*pentosans*) thus obtained is collected on cloth, washed and purified by repeatedly dissolving in dilute acid and reprecipitating with alcohol, this procedure being continued until the gum leaves a minimal ash on incineration.

To pass from the pentosans to the pentoses, the moist gum is hydrolysed (Conneler and Tollens, 1892 and 1903) by digestion for 12 hours with 25 parts of water and 2·5 parts of hydrochloric acid of sp. gr. 1·19, the mixture being finally heated on a water-bath until the furfural reaction (red coloration with aniline acetate paper) begins to make its appearance (about two hours). After filtration of the cold liquid and neutralisation with lead carbonate (testing with Congo-red paper), a few drops of barium hydroxide are added and the liquid filtered to remove precipitated lead chloride and barium carbonate. The solution is concentrated on a water-bath under reduced pressure, mixed with a little alcohol, filtered and concentrated to a syrup. This is taken up with methyl alcohol and the solution filtered to remove mineral and other impurities. The alcohol is then evaporated and the residue seeded with a few crystals of xylose or arabinose and left in a desiccator until the whole mass crystallises (this sometimes requires several weeks).

In order to separate the arabinose and xylose, which often occur together, Ruff and Ollendorff (1899) treat the mixed pentoses with eight times their weight of 75 per cent. alcohol and nearly their own weight of benzylphenylhydrazine dissolved in a little absolute alcohol. After several hours' rest with frequent shaking, there separates *arabinose benzylphenylhydrazone*, which, in the pure state melts at 174° and, when treated with excess of formaldehyde, liberates the arabinose; the latter is soluble in water, whilst formaldehyde benzylphenylhydrazone remains undissolved.

The aqueous arabinose solution, after separation and concentration to a syrupy consistency, deposits *pure arabinose* in crystals. The corresponding hydrazone of xylose is soluble in 75 per cent. alcohol, and yields xylose when decomposed with formaldehyde in the manner described above. The xylose can also be separated, according to Bertrand and Tollens (1900), by treating the mixture of pentoses with 2 parts of water, 1 part of cadmium carbonate, and 0·5 part of bromine. The mixture is heated for a short time on the water-bath, then left for 12 hours, evaporated, taken up with water, filtered, again evaporated, and mixed with alcohol ; this procedure yields crystals of *cadmium bromoxylonate*, $C_5H_9O_6BrCd$. Before carrying out this separation, however, it is necessary to make sure that the mixture contains no galactose or glucose. These sugars can be detected by oxidising the mixture with nitric acid (sp. gr. 1·15) on the water-bath and evaporating the liquid to two-thirds of its volume. If the liquid remains turbid in the cold, the presence of *mucic acid*, derived from *galactose*, is indicated, and if, after neutralising with potassium carbonate, acidifying with acetic acid and concentrating, potassium hydrogen saccharate separates, the presence of *glucose*—which gives *saccharic acid* on oxidation—is demonstrated.

meric; with more energetic oxidising agents, they give *trihydroxyglutaric acid*. On reduction they yield the corresponding alcohols, *arabitol* and *xylitol* (*see* pp. 225, 525), which are also stereoisomerides. By way of the corresponding cyanohydrins they can be converted into hexoses (*via* hexonic acids). All these reactions aid in establishing the constitution of these pentoses.

As they contain asymmetric carbon atoms, these sugars are optically active, and they exhibit the phenomenon of *mutarotation*; thus, for freshly prepared solutions of xylose, the value of the specific rotation is $[\alpha]_D = 75°$ to $80°$, while five minutes after the sugar is dissolved it has the stable rotation $+19°$.

When pentoses are boiled with dilute sulphuric acid or with hydrochloric acid of sp. gr. 1·06 (12 per cent.), they yield *furfural*, $C_4H_3O \cdot CHO$ (aldehyde), which distils over and gives a characteristic and intense red coloration with aniline and hydrochloric acid, a phenylhydrazone with phenylhydrazine, and a slightly soluble condensation product with phloroglucinol.[1]

Treatment of any pentose or hexose with caustic soda in presence of air or other oxidising agent (*e.g.*, HgO) yields no trace of saccharic acid, but gives formic acid and monobasic hydroxy-acids (*e.g.*, glycollic, dl-glyceric, trihydroxybutyric, and various pentonic and hexonic acids); if air is excluded, aldotetroses, formaldehyde, a little 2 : 3 -dienols, bioses, and glyceraldehyde are mainly formed.

Recent work has shown that the furfural obtained on distillation of vegetable substances with 12 per cent. hydrochloric acid is derived not merely from true pentosans, but also from oxycellulose, glycuronic acid, etc.; methylpentosans give methylfurfural. Hence Cross and Bevan suggest the name *furfuroids* for substances other than true pentosans which give furfural. On the other hand, it has been proposed by Tollens that the term *pentosan* be applied to the whole of the substances (furfuroids and true pentosans) which give furfural when distilled with 12 per cent. hydrochloric acid. *Hydroxymethylfurfural* (*see below*) does not distil in presence of acids but undergoes resinification, and hence escapes the Tollens method of estimating furfural.

Until comparatively recent times it was assumed that the pentosans were derived from the hexoses and polyhexoses, since it was known that 4-*hydroxymethylfurfuraldehyde*,

$$\underbrace{CHO \cdot C : CH \cdot CH : C}_{\text{———— O ————}} \cdot CH_2 \cdot OH$$

is obtained on heating levulose, d-mannose, d-glucose, d-galactose, chitose, etc., in a sealed tube with 0·3 per cent. of oxalic acid, while 4-*bromomethylfurfural*,

[1] *Quantitative Determination of Pentoses and Pentosans.* Flint and Tollens (1902) distil in a flask similar to that shown in Fig. 18 (p. 12), about 5 grms. of the substance with 100 c.c. of 12 per cent. hydrochloric acid, the heating being carried out in an oil-bath at 160°. Thirty c.c. of liquid are distilled over every 12 to 15 minutes, in which time 30 c.c. of fresh acid are added by means of a tapped funnel, this procedure being continued as long as the distillate reddens a strip of filter-paper moistened with an acetic acid solution of aniline. To the distillate is added an excess (double the amount of furfural expected) of pure phloroglucinol dissolved in 12 per cent. hydrochloric acid. The volume of the liquid is made up to 400 c.c. with the same acid in a graduated flask, which is well shaken and left for 12 hours, at the end of which time the precipitate is collected on a tared filter, washed with 150 c.c. of water, dried for four hours in an oven and weighed. The weight of furfural is obtained by dividing this weight by a variable factor, which has the following values for different amounts (in grms.) of the phloroglucinol compound: 0·20 grm. (1·820); 0·22 (1·839); 0·24 (1·856); 0·26 (1·871); 0·28 (1·884); 0·30 (1·895); 0·32 (1·904); 0·34 (1·911); 0·36 (1·916); 0·38 (1·919); 0·40 (1·920); 0·45 (1·927); 0·50 (1·930); 0·60 or more (1·931). The xylan is calculated by multiplying the quantity of furfural by 1·64, the araban by 2·02, while for mixed pentosans, the factor 1·84 is employed.

If the phloroglucide is formed in alcoholic solution, it may be estimated colorimetrically or spectroscopically (Pinoff and Gude, 1913).

Another method of procedure consists in precipitating the furfural with phenylhydrazine and estimating the nitrogen in the precipitate.

Jolles (1906), however, neutralises almost completely (to methyl orange) the distillate containing the furfuraldehyde, then adds 10 c.c. (more, if necessary) of a decinormal sodium bisulphite solution, and after two hours titrates the excess of bisulphite with a decinormal iodine solution (1 c.c. of which corresponds with 0·0075 grm. pentose).

Many plants contain methylpentosans as well as pentosans. The solubility of methylfurfural-phloroglucide in alcohol, in which furfuralphloroglucide is almost completely insoluble, serves as a means of estimating the former (Ishida and Tollens, 1911).

$$\underbrace{CHO \cdot C : CH \cdot CH : C}_{O} \cdot CH_2Br,$$

is obtained by heating levulose (or filter-paper, cotton, cellulose, straw, starch, dextrose, lactose, glycogen, etc.) under pressure with chloroform saturated at 0° with hydrogen bromide. Further, when the oxime of levulose is heated with concentrated caustic potash solution, the nitrile is first formed and then hydrocyanic acid and d-arabinose:

$$OH \cdot CH_2 \cdot [CH \cdot OH]_4 \cdot CH : NOH \rightarrow H_2O + OH \cdot CH_2 \cdot [CH \cdot OH]_4 \cdot CN$$
$$\rightarrow HCN + OH \cdot CH_2 \cdot [CH \cdot OH]_3 \cdot CHO.$$

Oxidation of d-gluconic acid with peroxides also gives d-arabinose.

Ketohexoses in general, when heated with *dilute* acids (*e.g.*, with 0·3 per cent. of oxalic acid under a pressure of 3 atmos.), are largely transformed into hydroxymethylfurfural, whilst the *aldohexoses* undergo this change only to a very slight extent; if mineral acids are used, or oxalic acid in larger quantity, levulinic acid is obtained instead of hydroxymethylfurfural.

U. Nef's work (1910) tends to show that, in plants, pentosans cannot be derived from the hexoses, but that they are formed rather from either aldotetroses and formaldehyde or 2-carbon-atom sugars and glyceraldehyde. The *hexoses*, in their turn, would be formed, not from pentoses and formaldehyde, but rather from 2 mols. of glyceraldehyde or 3 mols. of a 2-carbon-atom sugar, or even from 1 mol. of a 2-carbon-atom sugar and 1 of an aldotetrose.

XYLOSE is readily obtained by boiling with dilute sulphuric acid plants containing it, especially jute, bran, straw, or, better still, apricot stones or maize husks. It bears also the name of *wood-sugar*, and is yielded by the decomposition of gluconic acid.

When pure, it crystallises and forms a phenylosazone melting at 160°.

d-**ARABINOSE** is lævo-rotatory, but is obtained from calcium d-gluconate and hydrogen peroxide and from d-glucose. In the pure state if forms prismatic crystals.

i-**ARABINOSE** is the optically inactive racemic isomeride, and is found in the urine of persons suffering from *pentosuria*.

l-**ARABINOSE** is obtained by boiling vegetable gum with dilute sulphuric acid. It is dextro-rotatory, but is designated a lævo-compound because it is related chemically to l-glucose. It forms sweet-tasting crystals melting at 160°, and its phenylosazone melts at 157°.

Two other pentoses are: **RIBOSE**, which, with nascent hydrogen, gives *adonitol* (a pentahydric alcohol, $OH \cdot CH_2 \cdot [CH \cdot OH]_3 \cdot CH_2 \cdot OH$, and the only *sugar-alcohol* yet discovered in plants, the leaves of which are able to transform it into starch; the sap of *Adonis vernalis* contains as much as 4 per cent. of adonitol); and **D-LYXOSE**, which is obtained from galactonic acid and melts at 101°.

Higher homologues are the **Methylpentoses**: **FUCOSE**, contained in algæ; **CHINOVOSE, ISORHAMNOSE,** and **RHAMNOSE** (or **Isodulcite**), $C_5H_9O_5 \cdot CH_3$, which is obtained by boiling quercetin and certain other glucosides with dilute sulphuric acid.

According to Rosenthaler (1909), **Methylpentose** in presence of pentoses may be recognised by heating the solution for a few minutes on a boiling water-bath with HCl of sp. gr. 1·19 and observing the yellow liquid thus obtained in the spectroscope: methylfurfural, from methylpentose (even as little as 0·0005 grm.) gives absorption bands between the blue and green. The reaction is still more sensitive if a little acetone is added before heating, the liquid then being coloured red (by the methylfurfural) and giving a sharp absorption band in the yellow (D line); pentoses do not give this reaction if the liquid is heated. Other sensitive reactions are obtained with phloroglucinol, orcinol, resorcinol, pyrogallol, aniline acetate, etc.

HEXOSES, $C_6H_{12}O_6$

These are of frequent natural occurrence and exist as various optically active stereoisomerides, since they contain four asymmetric carbon atoms, while they also form inactive racemic compounds. They are substances of sweet taste, and are extremely soluble in water, but in alcohol they dissolve but slightly and in ether not at all; they crystallise with great difficulty and decompose

when distilled. Their phenylhydrazones are soluble, and their phenylosazones insoluble in water. When boiled with hydrochloric acid they all give (1) **Levulinic Acid** ($CH_3 \cdot CO \cdot CH_2 \cdot CH_2 \cdot CO_2H$), the silver salt of which forms characteristic crystals, and (2) a brown amorphous mass of so-called *humic substances.* With methyl alcoholic ammonia, the hexoses form **Osamines**, *e.g.*, **Glucosamine**, $C_6H_{11}O_5 \cdot NH_2$.

They reduce Fehling's solution or ammoniacal silver solution in the hot, and with oxidising agents they yield hexonic acids and then lower acids down to oxalic.

With lime they form additive compounds decomposable by carbonic acid; with boiling milk of lime they turn brown and give **Hexosaccharine** (lactone of saccharic acid), $C_6H_{10}O_5$. By the combined action of concentrated sulphuric and nitric acids, they are converted into *pentanitrates*, while with alcohols and gaseous hydrogen chloride they form ethers (*glucosides*). The aldohexoses give the fuchsine-sulphurous acid reaction (*see* p. 246), which is, however, not shown by the ketohexoses. The mode of formation of the phenylosazones is described on p. 524.

With hydroxylamine they form oximes, *e.g.*, *d*-**Glucosoxime**, which can be converted into the corresponding nitrile and then, by elimination of HCN, into the aldopentose (*d-arabinose*).

The hexoses are formed in various organisms and can also be obtained by hydrolysing polyhexoses with dilute acids or enzymes.

The optical activity of the hexoses indicated by the prefixes d-, l-, and i- indicates the sign of that of the substances with which they are connected genetically, but the fact that the actual direction of the rotation does not always correspond with this prefix is a source of some confusion. It must also be noted that the rotatory powers of the hexoses and pentoses are lowered when the sugars are dissolved in a centinormal alkali solution at 37°.

Synthetically the hexoses can be obtained from formaldehyde (*see* Note, p. 525), as well as from the hexahydric alcohols by gentle oxidation and from the hexonic acids by reduction. E. Fischer has synthesised d-glucose completely from glycerine, by way of (1) glyceraldehyde, (2) inactive fructose, which, with hydrogen, yields (3) inactive mannitol, oxidation of this giving (4) mannose and (5) racemic mannonic acid, the latter being resolved into its (6) active components by means of strychnine; d-mannonic acid, in presence of pyridine and water in the hot, produces (7) d-gluconic acid and this, on reduction, *d-glucose.*

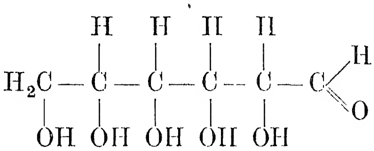
The relations between hexoses and pentoses were indicated in the Note on p. 527.

As was mentioned above, *fermentation* with yeast occurs only with d-glucose, d-fructose, d-galactose, d-mannose, and glycerose, no fermentation taking place with sorbose, the pentoses, l-glucose, l-fructose, l-mannose, or d-mannoheptose. Thus only the stereoisomerides of a certain group are fermentable.

The *structures* of the hexoses are deduced partly from their general reactions and partly from the following facts:

The *chain* of six carbon atoms in the hexoses is *normal*, since reduction with hydrogen yields a hexahydric alcohol, which is further reduced by heating with hydriodic acid to normal sec. hexyl iodide, $CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CHI \cdot CH_3$; the constitution of the latter is shown by the fact that the corresponding secondary alcohol is oxidised to n-propylacetone, $CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CO \cdot CH_3$, this, on oxidation, giving finally butyric and acetic acids of known constitution.

The hexoses contain five hydroxyl groups, as they yield pentacetyl-derivatives when boiled with acetic anhydride and sodium acetate or zinc chloride. Their constitutional formula hence cannot be other than:



since, if two hydroxyl groups were at any moment united with one carbon atom, a molecule of water would be eliminated immediately. Further, with hydrogen the hexoses form *hexitols*, which are not aldehydic but only alcoholic in character and do not give up H_2O under any conditions, so that two hydroxyl groups are not combined with one carbon atom. Neither can it be supposed that three hydroxyl groups are united with the terminal carbon, thus: $-\mathrm{C}\begin{matrix}\mathrm{OH}\\ \mathrm{OH}\\ \mathrm{OH}\end{matrix}$, because if this were so water would be readily separated and an acid formed, in which case the aqueous solution should conduct the electric current and have a dissociation constant much greater than that of acetic acid; but this is not found to be the case.

Combination with bases does occur (with the hexabioses), but the compounds formed are additive compounds.

Since then there are a number of different hexoses, all showing the same general behaviour, they must have the same constitution, the differences being due to differences in the spacial structure.

Theoretically, 16 active stereoisomeric aldohexoses are possible and have been already prepared. The rotatory powers of the *phenylosazones* and *phenylhydrazones* may be of opposite signs to those of the corresponding hexoses.

d-**GLUCOSE** (**Grape Sugar, Dextrose, Starch Sugar**), $C_6H_{12}O_6$, is an aldose found in abundance in grapes and many other sweet fruits in company with *d*-fructose; it also occurs in the urine of diabetic patients. It has a sweet taste, which is less intense (about two-thirds) than that of sucrose. It crystallises from water with $1H_2O$, which it loses at 120°, and from alcohol in the anhydrous form, melting at 146°. In aqueous solution it has the specific rotation + 53° at a temperature of 20°, but it exhibits mutarotation, the rotatory power being about double the above value in freshly prepared solutions which have not been boiled. Owing to its rotatory power glucose may be estimated polarimetrically (*see later*, Sugar). Yeast resolves it completely into alcohol and carbon dioxide.

When saccharose (a dextro-rotatory hexabiose) is heated with dilute acid, it is converted into a lævo-rotatory mixture of equal proportions of glucose (+) and fructose or levulose (−), which bears the name **Invert Sugar**,[1] the change being known as *inversion*, since it is accompanied by alteration of the sign of the optical rotation.

On oxidation, *d*-glucose gives *d*-**Gluconic Acid**, $OH \cdot CH_2 \cdot [CH \cdot OH]_4 \cdot COOH$, and then the dibasic **Saccharic Acid**, $CO_2H \cdot [CH \cdot OH]_4 \cdot CO_2H$, which, like tartaric acid, gives a slightly soluble acid potassium salt; the latter serves to characterise *d*-glucose, it being sufficient to oxidise with nitric acid and then precipitate the saccharic acid with saturated potassium acetate solution. When reduced, *d*-glucose yields *d-sorbitol* (hexahydric alcohol).

The sugar forms a phenylosazone, melting at 204° to 205°, and two phenylhydrazones, melting respectively at 115° and 144°.

When heated above 140°, glucose is converted into *caramel*.

In dilute solution it reduces Fehling's solution in the hot, and on this reaction is based the estimation of glucose.[2]

[1] **Invert Sugar**, of the consistency of honey, is a commercial product used by brewers and in making preserves, etc.; it is employed also to make artificial honey.

[2] **Estimation of Glucose.** In the chemical way the estimation is effected by means of Fehling's solution by the method described later in the section on Saccharose, about 10 grms. of solid glucose or 15 to 20 grms. of the syrupy product being dissolved in water, made up to 100 c.c. in a graduated flask and filtered through a dry, covered filter. Polarimetric estimation is not usually applicable, owing to the presence of dextrin, sometimes to the extent of 40 per cent., this increasing the rotation. The *dextrin* is determined by dissolving 5 grms. of the glucose in 400 c.c. of water, adding 40 c.c. of HCl of sp. gr. 1·125, heating for two hours on a boiling water-bath, cooling, neutralising exactly with NaOH and making up to 500 c.c. The total

Barfoed has proposed the following reaction for detecting the presence of minimum quantities of *glucose* (0·2 mgrm.) mixed with lactose, maltose, dextrin, and saccharose: to 5 c.c. of Barfoed's reagent (an acetic acid solution of normal cupric acetate) in a test-tube is added the dilute aqueous sugar solution (about 1 per cent.), the mixture being heated on a boiling water-bath for three and a half minutes, allowed to cool for 10 minutes, and filtered. If the filter retains red cuprous oxide, the presence of dextrose is demonstrated.

MANUFACTURE OF GLUCOSE. One hundred kilos of starch are mixed with 300 litres of boiling water containing 3 kilos of concentrated sulphuric acid, or 1 kilo of concentrated hydrochloric acid, and the mass heated in a suitable autoclave or converter (conical or cylindrical, capable of withstanding 6 atmos.), coated internally with lead and externally with insulating material. A current of steam is then passed in and the temperature raised to about 120° for an hour if liquid glucose, consisting one-half of glucose and the other of dextrin, or to 140° for 2 to 3 hours if crystallisable glucose containing only 30 per cent. of dextrin is desired. By allowing the steam to escape subsequently, the empyreumatic oils (which are of disagreeable odour) are carried away; the steam is condensed in cooled coils (the heat being used to heat water). The temperature of the mass is then maintained at 80° until a test portion gives no blue colour with iodine and no precipitate with lead acetate (or potassium silicate), these being indications of the saccharification of the dextrin and gummy matters; a further sign of this is the non-formation of a precipitate with alcohol.

The mass, at about 17° Bé. (= 30 per cent. of carbohydrates), is then decanted into the neutralisation vats, which are furnished with stirrers, and finely divided calcium carbonate, suspended in a large quantity of water, gradually added in order to neutralise and precipitate the sulphuric acid. After thorough mixing of the mass, it is allowed to settle and the liquid then decanted into another vessel, where the calcium sulphate remaining in solution is precipitated by the addition of a little ammonium oxalate. If hydrochloric acid were used, this is neutralised with sodium carbonate.

The liquid is next filter-pressed, evaporated in a vacuum to 30° to 32° Bé., decolorised in the hot by means of boneblack or dry blood mixed with powdered wood charcoal or by passing it through vertical filters filled with the charcoal similar to those used in sugar refineries. It is then concentrated in a vacuum (*see* Sugar Industry) either to 42° to 44° Bé., to give solid compact glucose separating in the cooling vats (fitted with stirrers), or to about 65° Bé., when ready formed crystals of glucose are added. The temperature is lowered to 18° to 20°, and after 3 or 4 days the separated crystals centrifuged and so freed from the syrupy portion, which retains the dissolved dextrin and other impurities. To obtain *granulated glucose* the solution is concentrated only to 32° Bé.; after 8 to 10 days in the cold, a granular *hydrated glucose*, $C_6H_{12}O_6$, H_2O, separates.

When a very dense liquid glucose (so dense that its specific gravity cannot be determined with the ordinary hydrometers) is required, a little dextrin is left in the sugar so as to prevent crystallisation.

The theoretical yield of pure glucose from 100 kilos of dry starch is 110 kilos.

In some factories the starch is saccharified with a little nitric acid, which gives a less highly coloured syrup and is more rapid in its action. The nitric acid is then eliminated by means of sulphurous acid, which is oxidised at the expense of the nitric acid to sulphuric acid, this being readily precipitable with lime.

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dextrose (including that formed by hydrolysis of the dextrin) in this solution is now determined by means of Fehling's solution. The difference between the amounts of glucose found before and after the action of acid, multiplied by 0·9, gives the quantity of dextrin. The acidity should not exceed 2 c.c. of normal caustic soda per 100 grms. of syrup. The proportion of *ash* varies from 0·2 to 0·7 per cent.

Solid commercial glucose contains 65 to 75 per cent. of glucose and the liquid 35 to 45 per cent. In pure solution, glucose may be estimated by means of the specific gravity:

Density at 17·5°	Degrees Bé.	Per cent. of pure glucose	Density at 17·5°	Degrees Bé.	Per cent. of pure glucose
1·0192	2·7	5	1·1310	16·4	35
1·0381	5·3	10	1·1494	18·8	40
1·0571	7·5	15	1·1680	20·6	45
1·0761	10·1	20	1·1863	22·7	50
1·0946	12·4	25	1·2040	24·4	55
1·1130	14·6	30	1·2218	26·1	60

The advantages of transforming starch into glucose by means of hydrofluoric acid consist in rapid and complete hydrolysis, ready separation of the whole of the acid as barium fluoride, and the production of a glucose with a pure flavour.

In 1901 Calmette found that, after heating crushed cereals with double the amount of 1 per cent. hydrochloric acid for one hour at 100°, one hour at 110°, and a third hour at 120°, and then cooling, the mass may be converted completely into glucose by the action of *Mucedineæ*.

USES. Large quantities of glucose are consumed for making sweet syrups, *caramel*,[1] fermented liquors, sweets and wine, preserving fruit, adulterating honey, dressing textiles, etc.

d-**FRUCTOSE** (**Levulose, Fruit-Sugar**) occurs abundantly, together with glucose, in sweet fruits, and is also found in large quantities in *honey* (which contains natural invert sugar). The hydrolysis of *inulin* (a polyhexose found in dahlia tubers) yields *d*-fructose alone. The sugar is *lævo-rotatory* and fermentable. It has the constitution of a *ketose*, $OH \cdot CH_2 \cdot [CH \cdot OH]_3 \cdot CO \cdot CH_2 \cdot OH$, hydrolysis of its cyanohydrin giving the heptonic acid,

$$OH \cdot CH_2 \cdot [CH \cdot OH]_3 \cdot \underset{\displaystyle COOH}{\underset{|}{C(OH)}} \cdot CH_2 \cdot OH.$$

The *phenylosazone* of *d*-fructose is identical with that of *d*-glucose.

Methylphenylhydrazine forms osazones only with ketoses and not with aldoses, with which, however, it forms colourless hydrazones, these being usually soluble and hence readily separable from the slightly soluble, intensely yellow osazones (*see* pp. 398 and 524).

When phenylosazones are heated gently with hydrochloric acid, they lose 2 mols. of phenylhydrazine with formation of *osones* which contain two carbonyl groups. Thus phenylglucosazone yields **Glucosone**, $OH \cdot CH_2 \cdot [CH \cdot OH]_3 \cdot CO \cdot CHO$, and this when treated with nascent hydrogen (from zinc and acetic acid) takes up 2H at the terminal carbon atom, fructose being thus obtained from glucose. On the other hand, reduction of a ketose gives the corresponding hexahydric alcohol, which, on oxidation, yields the monobasic hexonic acid; the latter loses water, giving rise to the lactone, and this gives the aldose on reduction. *d*-Fructose is laevo-rotatory; $[\alpha]_D = -92°$ at a temperature of 20°.

This sugar has been suggested for the use of diabetic and tuberculous patients and as a substitute for cane-sugar, since it is sweeter, and in syrups and honey it hinders the crystallisation of the other sugars.

In view of these uses, attempts have been made to prepare fructose industrially. König in 1895 and Steiner in 1908 proposed its extraction from endive roots and dahlia tubers (these contain from 8 per cent. to 17 per cent. of *inulin*). The crushed tubers are treated in the hot (below 65°) with a little milk of lime and with steam, and are then pressed. The juice, after defecation with clay, is allowed to crystallise in a rotating cooler, the mass of inulin crystals being centrifuged, redissolved in hot water, and converted into fructose by means of dilute acid (*see* Glucose); the fructose solution is concentrated in a vacuum. Steiner calculates that the sugar can be made by this process at a cost of 1*s*. per kilo.

A *characteristic reaction* for the detection of fructose in presence of other reducing sugars is obtained with the following solution: to a solution of 12 grms. of glycocoll in hot water are slowly added 6 grms. of pure cupric hydrate, the liquid being heated on a water-bath for about 15 minutes until complete solution takes place and then cooled to 60°; after 50 grms. of potassium carbonate have been added, the volume is made up to 1 litre and the whole filtered. This reagent is reduced in the *cold* only by levulose (1 to 5 per cent. solution), the time required varying from 4 to 9 hours; other sugars, including the pentoses, reduce it only at temperatures above 40°.

[1] **Caramel** (or *sugar colouring*) is prepared by fusing and heating glucose or saccharose at a temperature of 160° to 180° (not beyond this) in an iron vessel fitted with a stirrer. To glucose 1 to 3 per cent. of soda (ammonia is also largely used) is added to accelerate the operation and to neutralise the acid formed (saccharose also yields acid, being first partly inverted by the heating), and after the change is complete, 50 per cent. of hot water is added and the mass well mixed and filtered through charcoal. A brown, syrupy mass is thus obtained which is soluble in water or alcohol, giving a brown or yellow solution according to the dilution.

That obtained from saccharose, which does not contain dextrin and dissolves completely in 80 per cent. alcohol, is used for colouring spirits, whilst that from glucose, which contains dextrin and is entirely soluble in 75 per cent. alcohol, is used to darken beer and vinegar. The presence of more than 5 per cent. of ash indicates that a caramel has been prepared from molasses; good qualities contain only 1 per cent. of ash.

d-**MANNOSE**, $C_6H_{12}O_6$, is an aldose stereoisomeric with glucose, and is fermentable; it is obtained from mannitol, the corresponding alcohol, by oxidation. It melts at 136°, and differs from other monoses in forming a phenylhydrazone m.-pt. 195° to 200°, only slightly soluble in water. With oxidising agents it forms first monobasic *d-mannonic* acid and then dibasic *d-mannosaccharic* acid, $COOH \cdot [CH \cdot OH]_4 \cdot COOH$.

A general method for converting one hexose into a stereoisomeric one, *e.g.*, *d*-mannose into *d*-glucose, is as follows: the *d*-mannose is oxidised to *d*-mannonic acid and the latter dissolved in quinoline and the solution boiled; in this way the acid undergoes partial transformation into the stereoisomeric *d*-gluconic acid, reduction of the lactone of which yields *d*-glucose. The reverse change of *d*-gluconic into *d*-mannonic acid is also produced to some extent by boiling with quinoline, so that *d*-glucose can be converted into *d*-mannose. These sugars (and acids) differ only in the space arrangement of the groups united with the asymmetric carbon atom in the α-position, $OH \cdot CH_2 \cdot [CH \cdot OH]_3 \cdot \overset{\alpha}{C}H(OH) \cdot CHO$, since the phenylosazone of *d*-mannose is identical with that of *d*-glucose,

$$OH \cdot CH_2 \cdot [CH \cdot OH]_3 \cdot \underset{\underset{\displaystyle N \cdot NHC_6H_5}{\|}}{C} \cdot C : N \cdot NHC_6H_5.$$

It is this α-carbon atom, adjacent to the aldehyde group, which is influenced when a hexonic acid is boiled with quinoline or pyridine.

When glucose, fructose, or mannose is treated with a very dilute alkali solution, a mixture of all three sugars results. The fructose seems to be an intermediate product, since the dextro-rotation of mannose gradually changes to a lævo-rotation, owing to formation of fructose, the amount of the lævo-rotation subsequently diminishing as the fructose becomes converted into glucose.

l-**MANNOSE** and *l*-**GLUCOSE**, $C_6H_{12}O_6$ (**Aldoses**), are obtained together from *l*-arabinose by the cyanohydrin synthesis and reduction of the lactones of the resulting acids. Application of this synthesis to an aldehyde yields, in general, two optically active stereoisomerides, since a new asymmetric carbon atom is created and the chances of formation of the two isomerides are equal. The final mixture will, however, be inactive only when the initial molecule is inactive, while, when this is optically active (as with arabinose), the mixture will be active, as the components will not have equal and opposite activities; one of these will have a rotation greater than that of the original molecule by a certain amount and the other a rotation less by the same amount.

d-**GALACTOSE**, $C_6H_{12}O_6$ (**Aldose**), is obtained by oxidising dulcitol, $C_6H_8(OH)_6$, or by hydrolysing milk-sugar, in which case it is formed together with glucose. It melts at 168°, is fermentable, and exhibits mutarotation. It is an aldose, giving on oxidation first monobasic *d-galactonic acid* and then dibasic *mucic acid*, $COOH \cdot [CH \cdot OH]_4 \cdot COOH$, which is inactive.

HEPTOSES, OCTOSES, and **NONOSES** have not been found in nature, but are prepared synthetically from mannose by means of the cyanohydrin synthesis.

GLUCOSIDES

These are of frequent occurrence in the vegetable kingdom and, when heated with acid or alkali or subjected to the action of certain enzymes, decompose into a glucose and an alcohol (or phenol, aldehyde, or nitrogen compound); they are hence ethereal derivatives of the monoses (*e.g.*, **Amygdalin, Salicin, Populin, Coniferin, etc.**).

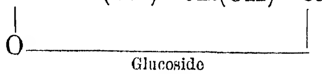
Artificial glucosides have been prepared by E. Fischer by the interaction of an alcohol and a monose in presence of hydrochloric acid (which withdraws water). The glucosides are analogous in structure to the *acetals*

$$R \cdot C\begin{cases} H \\ O \end{cases} + 2CH_3 \cdot OH = H_2O + R \cdot C\begin{cases} H \\ OCH_3 \\ OCH_3 \end{cases} \text{(acetal)},$$

but only 1 molecule of alcohol takes part in the reaction:

$$\mathrm{OH \cdot CH_2 \cdot CH(OH) \cdot \underset{\gamma}{CH(OH)} \cdot \underset{\beta}{CH(OH)} \cdot \underset{\alpha}{CH(OH)} \cdot CHO + CH_3 \cdot OH =}$$

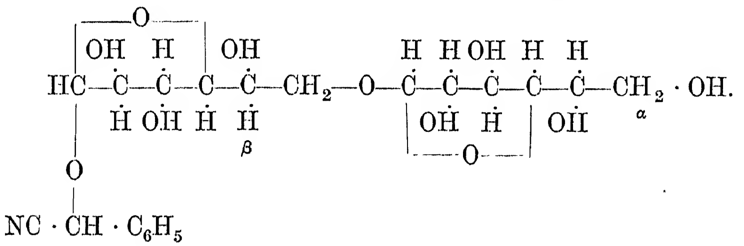
$$\mathrm{OH \cdot CH_2 \cdot CH(OH) \cdot \overset{\gamma}{CH} \cdot CH(OH) \cdot CH(OH) \cdot CH(OCH_3) + H_2O.}$$



Glucoside

The glucosides are readily resolved into their components, so that union of these directly through carbon atoms is excluded. The combination with the oxygen of the hydroxyl in the γ-position is deduced from analogous reactions, such as formation of lactones. The constitution of bioses is explained similarly (*see later*).

According to Auld (1908) the constitution of **Amygdalin** is as follows:



Ciamician and Ravenna (1908) showed that, when glucosides are introduced into plants (maize and beans), they are absorbed and transformed without producing any effect, whilst the decomposition products of the glucosides (benzaldehyde, salicylic alcohol, hydroquinone, etc.) act as poisons. Hence the formation of glucosides in plants seems to have the effect of paralysing the poisonous action of certain substances. The same authors (1909) found that, when maize is made to absorb *saligenin*, this is partly transformed into its glucoside, *salicin*; in a similar manner they obtained *benzylglucoside* (1911).

B. HEXABIOSES

Almost all the bioses at present known decompose into hexoses (either two different monoses or 2 mols. of one and the same monose). No biose gives a hexose and a pentose.

This decomposition of bioses, which is known as *hydrolysis*,

$$C_{12}H_{22}O_{11} + H_2O = 2C_6H_{12}O_6,$$

can be effected by boiling with dilute acid or by the action of enzymes, and since it takes place with great readiness, it is assumed that the constituent monoses of the bioses are united, not between carbon atoms, but more probably between oxygen atoms. It would appear, however, that the hydrolysis is not a monomolecular reaction (*see* Vol. I., p. 69).

Synthetic bioses are obtained by treating, for instance, a hexose with acetyl chloride, the resulting *acetochlorhexose*, in presence of sodium alkoxide and a hexose, giving the acetyl derivative of a biose; elimination of the acetyl group by means of soda then yields the biose itself.

Bioses may also be obtained by the action of certain enzymes on monoses; thus, with *maltase*, glucose gives *isomaltose* (not, as was formerly thought, maltose; *see* p. 126). The *lactase* of kephir acts on a mixture of glucose and galactose, giving *isolactose*: with glucose alone it yields a different biose. Glucose and galactose may also be condensed by the action of *emulsin* (*see* p. 136).

Of the hexabioses, maltose, lactose, and saccharose will be considered (for *melibiose*, *see later*, *under* Raffinose).

MALTOSE forms crystals of the formula $C_{12}H_{22}O_{11} + H_2O$ and is strongly dextrorotatory. As was seen in considering the manufacture of alcohol and of beer, it is prepared industrially from starch by the action of diastase (see pp. 133, 134, 141).

Hydrolysis of maltose by dilute acid yields only *d*-glucose. It gives reactions similar to those of the monoses. Thus, it reduces Fehling's solution, and with phenylhydrazine forms phenylmaltosazone, $C_{24}H_{32}O_9N_4$. On oxidation it yields monobasic **Maltobionic Acid**, $C_{12}H_{22}O_{12}$, which gives *d*-**Gluconic Acid**, $OH \cdot CH_2 \cdot [CH \cdot OH]_4 \cdot COOH$, on hydrolysis. Hence maltose contains only one carbonyl group and not the two corresponding with the 2 constituent glucose molecules, the phenylosazone being formed with 2, and not 4, mols. of phenylhydrazine, while oxidation of the sugar yields a monobasic and not a dibasic acid. Hence the 2 mols. of glucose in the maltose molecule are joined in such a way that only one carbonyl group remains free to exert its characteristic reactions, the other serving to link up the 2 glucose molecules. It is usual to include between brackets the monose residue which has no free carbonyl owing to the oxygen atom of this group being joined to the other monose residue, and to place outside the brackets those monose residues which retain free carbonyl. Maltose would then be represented by the formula $\underset{d\text{-glucose}}{(C_6H_{11}O_5 \cdot O)}\ \underset{d\text{-glucose}}{C_6H_{11}O_5}$. Maltose is not fermentable directly, the maltase of yeast first converting it into fermentable glucose (see p. 134).

Isomaltose is not fermentable and has $[a]_D + 70°$; with phenylhydrazone it yields soluble phenylisomaltosazone.

LACTOSE (or **Milk-Sugar**), $C_{12}H_{22}O_{11} + H_2O$, is contained in milk (up to 5 per cent.) and is less sweet than cane sugar. Its reactions are similar to those of the monoses (reduces Fehling's solution, etc.), and it yields *d*-glucose and *d*-galactose on hydrolysis. It does not ferment with beer yeast, which contains no enzyme capable of hydrolysing it. The glucose residue has its carbonyl free, whilst the carbonyl of the galactose takes part in the union of the 2 monose molecules, so that it will be represented thus: $\underset{d\text{-galactose}}{(C_6H_{11}O_5 \cdot O)}\ \underset{d\text{-glucose}}{C_6H_{11}O_5}$.

In fact, oxidation of lactose by means of bromine water results in the formation of monobasic *lactobionic acid*, which, on hydrolysis, gives *d*-galactose and *d*-gluconic acid. Cold water dissolves 16·6 per cent. and boiling water 40 per cent. of the sugar.

INDUSTRIAL PREPARATION. Unless a dairy has an average production of at least 60 to 80 hectols. of whey per day, it is not expedient to extract the milk-sugar. The preparation is now carried out as follows: The whey is treated immediately after the first coagulation of the cheese.[1] The concentration is carried out in single or double-effect vacuum pans, similar to those used in sugar factories. Whey is passed continuously into the concentrator until the liquid attains a density of 30° Bé. in the hot (about 60 per cent. of the sugar). It is then collected in iron vessels holding about 700 litres, in which it is cooled by water circulating through a surrounding jacket. In the course of 24 hours, during which the mass is well stirred three or four times, the temperature is lowered to 20°. A pasty mass of fine crystals then separates, with an oily layer at its surface.

The crystals are separated by diluting the mass with a little cold water ($\frac{2}{5}$) and centrifuging, the crystals being retained in the drum of the centrifuge by means of a cloth. When a sufficient quantity of crystals has been thus collected in the basket of the centrifuge, the mass is washed with a gentle spray of cold water, the crude, slightly yellow sugar thus obtained representing 3·6 to 4·3 per cent. of the whey taken.

This *crude milk sugar* contains 88 per cent. of sugar and 12 per cent. of water and various impurities (proteins, etc.) The liquid from the centrifuge still contains about 30 per cent. of the total sugar (not crystallised but forming a syrup). This liquid, which usually has a *density* of about 15° Bé., is heated to boiling by direct steam in a vessel with a flat, perforated false bottom, the albumin being thus coagulated. After half an hour's rest, the albumin collects as a compact layer at the surface, the liquid being then drawn off from below so as to leave the cake of albumin on the false bottom; this is removed, pressed in bags, and given to pigs or mixed with white flour to make bread. The albumin-free liquid is concentrated in vacuum pans to 35° Bé. (measured in the hot) and allowed to cool for several days, with occasional stirring, in iron vessels. This procedure yields a dark pasty mass of the crystalline sugar, which is collected by diluting with a large quantity of *cold* water and centrifuging as before; this sugar amounts to 0·3 to 0·7 per cent. of the original quantity of whey.

[1] Dairies not producing sufficient whey simply purify it by boiling with acid whey to coagulate the albumin, and filtering. It is then despatched to works which treat it further.

The *mean* yield of crude milk-sugar is 4·3 per cent. of the whey (the maximum of 4·8 per cent. being obtained in winter and the minimum of 3·9 per cent. in summer).

The liquid from the second crystallisation and centrifugation is not treated further, unless by osmosis; it is preferably utilised as cattle-food, as it is rich in potassium salts, nitrogen, and phosphoric acid.

The crude sugar is either dried and placed on the market or subjected to a refining process. If left in heaps, it deteriorates to some extent.

The *refining* is carried out as follows: The sugar is dissolved, in an open boiler with a double bottom (heated by indirect-fire heat), in water at 50°, the liquid being well stirred so as to obtain a solution of 13° to 15° Bé. (24 to 27 per cent. of sugar). A little bone-black, or fuller's earth (*see* p. 490), and about 0·2 per cent. (on the weight of sugar) of acetic acid are then added, and the heating continued until the boiling-point is approached, when magnesium sulphate (about 0·2 per cent.) is added and the liquid subsequently kept boiling for a few minutes. The mass suddenly froths very considerably (if necessary, the steam-cock is closed; the boiler should not be too full initially) and the temperature rises to 102° to 105°. The charcoal decolorises the liquid and absorbs unpleasant flavouring substances, while the albumin is coagulated in large flocculent masses (by the acetic acid) and the phosphoric acid is precipitated by the magnesium. The hot liquid is filter-pressed, and the solid residue, after being washed with water and treated with a suitable amount of sulphuric acid, constitutes an excellent nitrogenous superphosphate. The clear liquid from the filter-press is concentrated as usual *in vacuo* to 35° Bé. in the hot (65 per cent. of sugar), the formation of froth being prevented. It is then crystallised, and when the maximum quantity of crystals has separated, these are separated by centrifuging, giving *first product.* After subsequent concentrations of the mother-liquor, *second* and *third* products are obtained. These three products together amount to about 3 to 3·5 per cent. of the original quantity of whey; they may be kept separate or mixed and then recrystallised.

To obtain the sugar in the very white powdery form in which it is now sold, the refined product (first, second, or third) is dissolved in hot water to give a solution of 15° Bé., which is boiled, and, after a little aluminium sulphate (0·1 per cent.) has been added, filter-pressed, the clear watery filtrate being concentrated to 32° Bé. It is then crystallised in copper vessels, centrifuged, and dried in revolving inclined drums round which hot water passes.

It is dry when it no longer adheres when compressed between the hands. The *cold* sugar is ground and sieved to an impalpable powder. The average yield over the whole year is 2·5 kilos of the powdered sugar per 100 litres of whey. This powder should be left in open vessels for some days, as, if packed immediately, it develops an unpleasant smell (which, however, it loses if spread out in the air).

To obtain the sugar in masses of aggregated crystals, solutions of the gravity 21° to 24° Bé. are crystallised in wooden vessels containing numbers of small wooden rods; the crystallisation sometimes occupies as much as a fortnight, and a liquid of 13° Bé. remains which can be concentrated anew.

The *albumin* separated when whey is boiled contains, after pressing, about 60 per cent. of water and 40 per cent. of dry matter composed of 17 per cent. of protein substances, 11 per cent. of milk-sugar, 2·3 per cent. of fat, 5 per cent. of ash (one-half of which is insoluble in water), and 1·7 per cent. of lactic acid.

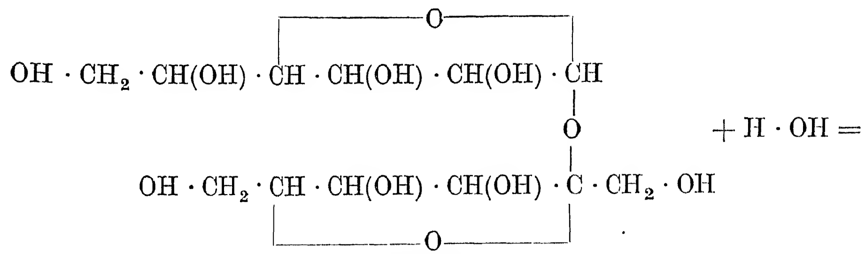
The final mother-liquor, or *lactose molasses*, is brownish black, and contains about 73 per cent. of water, 6 per cent. of ash (two-thirds soluble in water), 0·10 per cent. of fat, 0·6 per cent. of nitrogen, 1·5 per cent. of acid (calculated as lactic acid), and 22·5 per cent. of substances which reduce Fehling's solution (calculated as milk-sugar).

The pre-war price varied from £34 to £48 per ton.

Tests for Milk-Sugar. Adulteration with mineral substances is recognised by the ash exceeding 1 per cent. in amount. When dextrin is present, this does not dissolve in alcohol, while the presence of glucose or saccharose (even as little as 2 per cent.) is indicated by evolution of carbon dioxide from a 10 per cent. solution of the sugar mixed with a little (0·2 grm.) fresh pressed beer-yeast and kept at 20° to 30° for two days; the invertase present in the yeast inverts the saccharose, which then ferments, but it does not break down the lactose, which consequently does not ferment. It is also found that when the *Bulgarian ferment* (*Bacterium bulgaricum*) acts on a mixture of saccharose and lactose, the latter alone is destroyed.

SACCHAROSE (Sucrose, Cane-sugar), $C_{12}H_{22}O_{11}$

Saccharose may be regarded chemically as the condensation product of two hexamonoses, glucose and fructose, which are generated by hydrolysis with dilute acid. The characteristic reactions of the monoses are lacking in saccharose, which does not reduce Fehling's solution, form osazones, or turn brown when treated with caustic soda solutions. It must therefore be assumed that the saccharose molecule contains no free carbonyl group (aldehydic or ketonic), the two such groups in the two monoses being annulled in the condensation. This is seen clearly from the following equation, in which a constitutional formula with the lactonic groupings so common to these substances (*see* p. 526) is attributed to saccharose :



Saccharose

$$OH \cdot \underset{\text{Glucose}}{CH_2} \cdot [CH \cdot OH]_4 \cdot C\begin{matrix} \diagup O \\ \diagdown H \end{matrix} + OH \cdot CH_2 \cdot \underset{\text{Fructose}}{[CH \cdot OH]_3} \cdot CO \cdot CH_2 \cdot OH.$$

The rational formula (*see* Maltose) of saccharose will hence be :

$$(C_6H_{11}O_6 \cdot O \cdot C_6H_{11}O_5).$$

Saccharose and the bioses generally are not changed by the direct action of alcoholic ferments or of the majority of enzymes, so that they cannot be converted immediately into alcohol and carbon dioxide, as is the case with the hexoses. In order that alcoholic fermentation of cane-sugar may take place, it is necessary that the sugar should be first inverted by the *invertase*—almost always present in yeasts—into fermentable glucose and fructose. Hence, yeasts which contain no invertase cannot ferment saccharose. *Saccharomyces octosporus*, for instance, leaves this sugar unchanged, although it ferments maltose, owing to the presence of *maltase*, which hydrolyses the maltose to glucose.

It has already been mentioned that saccharose is readily hydrolysed by heating it with a very small quantity of a dilute mineral acid, and that this hydrolysis is known as *inversion* (*see* pp. 531, 533) because the dextro-rotatory saccharose ($[\alpha]_D = +66 \cdot 5°$) is changed into a lævo-rotatory mixture of equal proportions of glucose and fructose (*invert sugar*). The *velocity of inversion*, s, is proportional to the amount of cane-sugar present in the solution at any moment, and is hence expressed by $s = k\ (p - x)$, where p is the quantity of the original sugar and x that which has already undergone inversion. The *inversion constant*, k, varies with the nature of the acid employed and is proportional to the degree of electrolytic dissociation of the acid, the rate of inversion increasing with the number of free hydrogen ions. It is, indeed, possible to determine the *ionic concentration* of an acid solution by means of the velocity of inversion, or the amount of reducing sugar formed in unit time, in a saccharose solution of definite concentration. In the cold, sulphurous and carbonic acids have scarcely any inverting power.

Saccharose melts at 160° and, on solidification, forms an opaque, amorphous, glassy mass, which then crystallises in inclined monoclinic or rhombic prisms with blunted angles ; at a higher temperature it caramelises to a brown

mass with evolution of gas (*see* p. 533). It has the sp. gr. 1·5813. When heated for a long time at 180° to 220°, it yields acetone.

One part of water dissolves 2·5 parts of saccharose at 0° and 4·5 parts at 100°. It is almost insoluble in absolute alcohol or ether, but dissolves slightly in methyl alcohol. It readily forms supersaturated aqueous solutions, which then rapidly deposit anhydrous crystals; this phenomenon is utilised in its industrial preparation.

Cane-sugar forms compounds (*sucrates*) with inorganic bases; thus, with lime it forms (1) **Monocalcium Sucrate,** $C_{12}H_{22}O_{11}$, CaO, $2H_2O$, soluble in water, (2) **Dicalcium Sucrate,** $C_{12}H_{22}O_{11}$, $2CaO$, also moderately soluble in water, and, on heating a solution of either of these compounds, (3) **Tricalcium Sucrate,** $C_{12}H_{22}O_{11}$, $3CaO$, $3H_2O$, insoluble in water.

A sensitive reaction for the detection of small quantities of sugar is indicated on p. 533.

Pozzi-Escot (1909) has devised a still more sensitive reaction for the sugars: into a test-tube are introduced 2 c.c. of the aqueous solution, 1 c.c. of 5 per cent. ammonium molybdate solution and, after mixing, 10 to 12 c.c. of concentrated sulphuric acid, which is poured carefully down the side of the tube. The formation of a blue ring within 20 minutes indicates the presence of more than 0·0005 per cent. of sugar, and if the blue ring appears within 30 minutes when the upper part of the liquid is heated to boiling, the solution contains at least 0·00002 per cent. of sugar.

INDUSTRIAL PREPARATION OF SACCHAROSE [1]

Saccharose is contained in varying quantity (5 to 20 per cent.) in different vegetable organisms. For instance, the sugar-cane (*Saccharum officinarum*)

[1] **History of Beet-sugar.** The first saccharine material worked and utilised by man as food was probably honey. The sugar-cane was known to the ancient Chinese, the Indians, and also the Persians and Arabs 200 years before Christ and only later was it introduced into Egypt, Greece, and Sicily; the medicine-men of this epoch employed cane-juice and honey as medicine. In the seventh century sugar in the solid form was an article of commerce, and in the eighth century the Persians extracted it from the sugar-cane and prepared it in cakes; after the ninth century, the cultivation of the cane was extended by the Arabs to Egypt, Syria, Crete, Sicily, and Spain. In the fifteenth century, the Portuguese introduced the culture into Madeira and Brazil, while the Spaniards carried it to the East Indies and the Canary Islands, and the Dutch to Java and Guiana. At the present time the sugar-cane is largely cultivated in Cuba, Java, Manila, Martinique, Jamaica, Louisiana, Brazil, Peru, China, Japan, India, Egypt, and part of Australasia. In Europe it is grown to a small extent only in Spain.

In 1806, when France and the allied nations established the Continental blockade against England (lasting until 1814) and the supply of Colonial sugar furnished by England to the whole of Europe hence failed, attempts were made to discover a substitute for cane-sugar.

As early as 1705 the French agriculturist, Olivier de Serres, had observed that the beet contained a considerable proportion of sugar, and in 1747 the Berlin pharmacist, Sigismund Marggraf, attempted the extraction of the sugar, obtaining a yield of 6 per cent., but at that time it could not compete with the much cheaper Colonial sugar. Carl Achard, a pupil of Marggraf, after 20 years of experimental work on the selection of the best qualities of beet, etc., erected a factory for the manufacture of beet-sugar at Kunern, in Silesia (1801), but it was not found possible to extract more than 3 per cent. of crystalline sugar, which did not cover the expenses, so that the factory was closed. Achard, however, continued to perfect his process, and when the Continental blockade produced in 1811 a tenfold increase in the price of sugar, several beet-sugar factories were started in Germany, but these were still so imperfect that they were obliged to suspend operations when the blockade ceased. At this same time Napoleon I. induced the most eminent scientific and technical men in France to apply themselves to this problem, and the extraction processes were rapidly improved, machines being devised for rasping and pressing the beets. With the introduction of the use of steam for concentrating the juices and of granulated bone-black for decoloration, beet-sugar began to compete seriously with Colonial sugar, even after the raising of the blockade. In 1828 there were indeed 58 large and flourishing factories in France, producing annually 30,000 tons of sugar. Napoleon I. had distributed in prizes to encourage this industry the sum of £40,000 and had himself erected four factories and brought 32,000 hectares of land under beet cultivation.

In Germany the sugar industry was started again in about 1836, especially in the neighbourhood of Magdeburg, where a fortunate choice was made in the quality of beet employed, the lot of the agriculturist—at that time depressed owing to poor grain crops—being thus greatly ameliorated. The further development of this industry was favoured by protective duties imposed by the Government, in France—until a few years ago—and in Germany and Austria,

gives 15 to 20 per cent.; the beetroot (*Beta vulgaris*), 7 to 17 per cent.; *Sorghum saccharatum*, 7 to 12 per cent.; the pineapple, 11 per cent.; strawberries, 5 to 6 per cent.; maize stems, sugar maple, etc., also contain small proportions of saccharose. Most sweet vegetable juices, however, contain glucose (grape-sugar) and levulose. The plants employed industrially for the extraction of sugar are the maple, sugar-cane, and beetroot. Unsuccessful attempts have been made with maize stems, which contain as much as 14 per cent. of sugar when the unripe heads are cut, but the sugar extracted sometimes contains 12 per cent. of invert sugar and other impurities.

I. **ACER SACCHARINUM NIGRUM** (Sugar Maple), which is largely cultivated in Canada, and, to a less extent, in the United States, yields a sap containing a considerable proportion of sugar. The sap is withdrawn from the living tree by means of two or three holes bored in the stem a few feet above the ground, a metal tube fitted into each hole commanding a tinned-iron vessel. From these vessels the sap is collected twice a day during the sugar season, which lasts for about three weeks in the year. A single tree yields from 12 to 24 gallons of sap each season, and from 4·5 to 6 gallons of the sap give 1 lb. of maple sugar. In some cases the sap is treated with chemical agents which precipitate certain of the impurities, but usually the sap is concentrated and crystallised directly, since the commercial value of the sugar depends principally on the flavour due to the "non-sugars" or impurities present. In Canada the industry flourishes mainly in the province of Quebec, where the output of the sugar amounted to 13,000 tons in 1919 and to 13,400 tons in 1920.

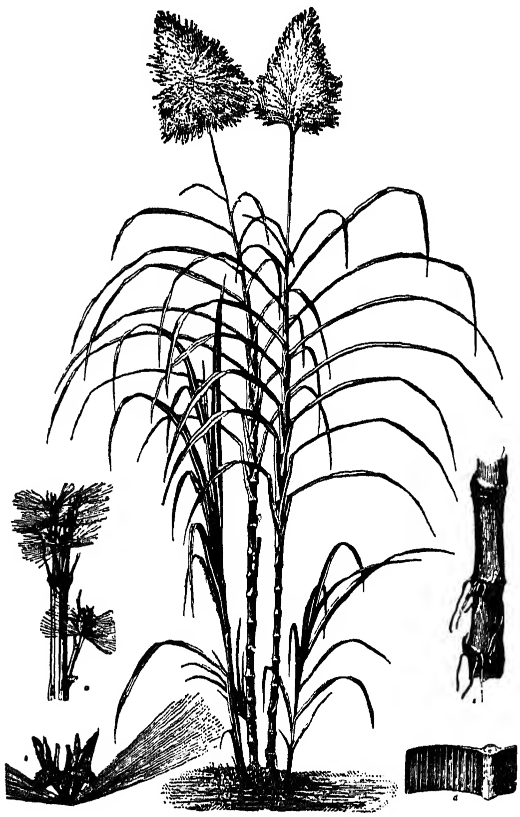


FIG. 310.

II. **THE SUGAR-CANE** is the principal source of Colonial sugar.

It is a plant (*Saccharum officinarum*, Fig. 310) which has been cultivated from the most remote times in India, Persia, and Arabia, whence it passed into Egypt and Greece. At the time of the Normans it was cultivated in Sicily, and from there it was introduced in 1420 into Portugal and Spain, and thence into the West Indies; the Dutch carried it to the East Indies, where its development was very rapid. At the present time it is cultivated most widely in Cuba, Porto Rico, San Domingo, Havana, Brazil, and the East Indies (Bengal, Java, and the Philippines).

The plantations are made with shoots from the living plant (obtained from seed), these being placed about 1 metre apart and weeded after four to five months. The cane begins

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where the prosperity of the sugar factories is continually increasing. The industry then developed in Belgium and Russia, while in Italy it was initiated only towards the end of the last century. In England the cultivation of the sugar-beet has been attempted, apparently with success, on a small scale only during recent years.

In 1855 the world's production of beet-sugar already amounted to 1,500,000 tons, and in 1900 Central Europe alone produced 8,500,000 tons. During the same lapse of time the output of cane-sugar increased only from $1\frac{1}{2}$ to $2\frac{1}{2}$ millions of tons.

to sprout in 12 months and requires a further six months to mature, when it has a yellowish colour and is 3 to 6 metres high and 4 to 6 cm. in diameter ; it sometimes reaches a weight of 9 kilos.

The stem and roots of each plant will yield cane for twenty consecutive years without renewal. The negro labourers remove the head (used for cattle-food) from the cane with a blow from a scythe, and with another sever the cane at the base ; the leaves (used for thatching) are then removed, and the cane worked up each day, as it rapidly ferments if left in heaps. The omnivorous ant is the enemy most feared by the planter. At one time the bundles of cane were crushed in a primitive mill formed of three vertical cylindrical tree-trunks, shod with iron and worked by water-wheels or horses, but nowadays use is made of three horizontal cylinders, the distances between which can be regulated so as to vary the pressure (Fig. 311).

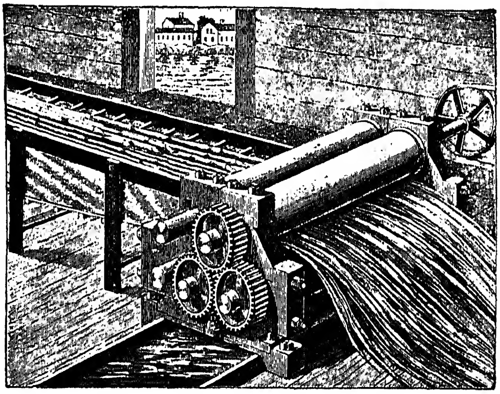

FIG. 311.

In large factories use is made of batteries of these three-cylinder groups (Fig. 312), the cane being passed from one group to the next by means of an endless band. Prior to this the cane is treated in a *crusher* (Fig. 313), consisting of two toothed rolls.

The liquid thus expressed is termed *raw juice*, and the woody residue *bagasse* or *megass*. After each pressing the cane is moistened with water and finally contains 1 to 1·5 per cent. of sugar. In Mexico bagasse and the leaves of Henequen plants are now used for the manufacture of spirit. The total juice, including that from the second pressing, forms about 90 per cent. of the weight of the cane and contains 15 to 19 per cent. of sugar. In the East Indies, owing to irrational methods of working, more than one-half of the sugar is lost,

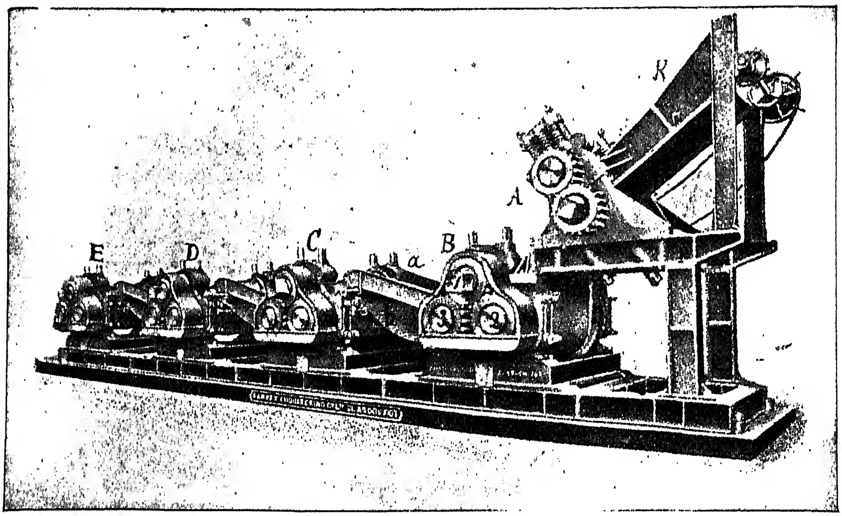

FIG. 312.

whilst in Brazil, where improved processes are in use, more than 60 per cent. of pure sugar is obtained.[1] In North America the diffusion process has been introduced, and the loss of

[1] The following information has been furnished by Alberto Bianchi, who visited (in 1911) various cane-sugar factories in South America. The most important centres in South America

sugar reduced to less than 20 per cent. ; diffusion has also been tried in Brazil, but was abandoned owing to its expense, especially as regards fuel.[1] Treatment of the fresh juice with a considerable amount of sulphur dioxide is often employed to prevent the ready fermentation which otherwise occurs. Attempts have also been made to decolorise with sodium hydrosulphite.

Even recently cane-sugar constituted about one-half of the total sugar produced, but it is nearly all consumed where grown in a more or less refined condition, whilst a very large trade is done in beet-sugar in a highly refined form, and in some cases this sugar competes with cane-sugar in districts where the latter is produced. The output of cane-sugar in Cuba alone was 700,000 tons in 1898 and 1,050,000 in 1904. In order to encourage the cultivation of the sugar-cane, the United States Government have instituted a system of bounties (as much as 5*s*. 6*d*. per cwt.), and in 1910 paid £13,800,000 in this way; in addition to this there is a protective duty of 24*s*. per quintal on the sugar, this being paid by the consumer. In the East Indies the production increased to 2,166,000 tons in 1904. (The European output of beet-sugar is about 8,000,000 tons per annum.)

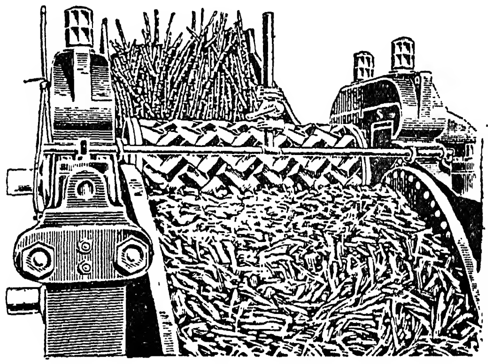

Fig. 313.

for the production of the sugar-cane are: in Brazil, the States of Pernambuco, Bahia, Rio de Janeiro, and San Paulo, and, in a less degree, Maccio and Maranhao; in Argentine, much cane-sugar is produced in the northern provinces, especially in Tucuman. The varieties of cane most widely grown in Brazil have been imported from Java and Haiti and yield from 10 to 17 per cent. of crystallisable sugar. The works are erected in the plantations, and the more primitive ones, in which the juice is still concentrated under the ordinary pressure, are called *Engenhos*, whilst those furnished with modern machinery and multiple-effet vacuum plant are termed *Usinas*.

In the *Engenhos*, the broken cane is crushed between wooden rollers worked by oxen or horses. When the juice is not defecated, it is concentrated in large copper pans heated by direct fire, and is then left to crystallise in wooden vessels, the molasses being subsequently decanted off and the crystalline mass placed to drain in barrels with perforated bottoms. When defecation is employed, the juice is boiled with lime and skimmed several times, the defecated juice then passing into a series of two or three pans, each lower than the preceding one; in the last of these the desired concentration is attained. The sugar thus obtained is always moist, owing to the residual molasses, and varies in colour from yellow to brownish black; the yield is less than 6 per cent.

In the *Usinas*, where the yield may amount to 10 to 11 per cent. (by the wet process, or 7 to 9 per cent. by the dry process, or 6 per cent. when the cane is pressed in a single pair of rolls), the canes are pressed between three pairs of double rollers by hydraulic pressure, poorer juice (wet process) being gradually sprayed on to the partially pressed cane; the pressed cane is used as fuel. The juice, with a density of 5° to 10° Bé., is pumped to the sulphitation tanks (sulphur dioxide or calcium bisulphite is used; but this is not done in all factories) and thence passes to copper vessels with spherical bottoms and holding 2000 to 4000 litres. In these it is defecated with milk of lime, being heated by steam coils and skimmed once or twice. After carbonation, the juice is transferred to other vessels of about the same size as the former ones and placed at a lower level; in these it is again boiled and skimmed. It is next removed to the depositing tanks and, after some hours, is pumped to the triple-effet vacuum concentrators, from which it passes at 23° to 26° Bé. to copper boilers of 2000 to 4000 litres capacity (clarifiers), where it is boiled by means of steam coils for about half an hour—until it ceases to form scum (which is removed). The juice is next boiled in a vacuum apparatus, in which crystallisation commences; the subsequent treatment and refining of the sugar are carried out as in beet-sugar factories (*see later*).

In many factories, the yield of white, first-jet sugar is increased by decolorising the juice, not by sulphitation, but by the addition of *blankite* (*sodium hydrosulphite*) in the proportion of 300 to 500 grms. per ton of sugar; this is added partly to the clarifier and partly to the concentration vessel.

It is calculated that the cost price (pre-war) of cane-sugar in the factory, without reckoning interest on capital, was £7 12*s*. per ton in Java, £9 4*s*. in Cuba, and £12 8*s*. in Hawaii.

[1] Since 1910 attempts have been made, especially in Cuba, to utilise the bagasse for the preparation of cellulose, the sugar being extracted by the diffusion process.

Cane-sugar molasses is of value owing to its agreeable flavour and smell, and it is therefore converted, by fermentation and distillation, into *rum*, that of Jamaica being especially renowned.

III. The **BEETROOT** was formerly an annual, but became changed by selection into a biennial, giving flowers and fruit (or seeds) only in the second year. Different varieties of *Beta vulgaris* or *Beta maritima* (Linnæus) are now grown. The original wild varieties contained only 5 to 6 per cent. of sugar, but after careful and repeated selection during a period of 25 years, varieties have been obtained which, under the most favourable conditions, contain as much as 18 per cent. of sugar.[1]

Nearly all of the best varieties now cultivated are derived from the Klein-Wanzleben. The shape of the root is of considerable importance. Thus, the rounder beets are generally rich in sugar but give a small crop; roots of oblong and swollen form crop well but are poor in sugar; whilst fusiform roots which are not too smooth and have little top and tail (waste products of the sugar factory) are the ones preferred by the agriculturists and manufacturers (*see* Fig. 314).

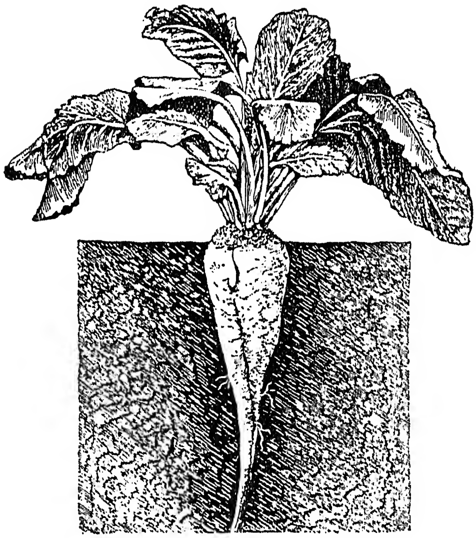

FIG. 314.

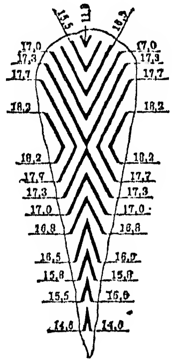

FIG. 315.

Value attaches, besides to the shape, also to the specific gravity, and still more to the sugar-content. Fig. 315 shows the saccharine content of the various zones composing the beetroot. It will be seen that the richness in sugar diminishes from the centre to the periphery, and especially to the top and tail, which also give the more impure juices.

[1] Achard himself recognised varieties of the beet best adapted for the manufacture of sugar, but it was Vilmorin, in France, who in 1856 rationally selected the first variety rich in sugar (*Vilmorin's white*) by repeated reproduction of the roots with the highest saccharine content; this he arrived at by immersing the roots in saline solutions of different concentrations so as to determine their specific gravities, from which he deduced the content of sugar. Later, however, Scheibler showed that there is not always proportionality between the specific gravity and saccharine value.

In Germany, more rigorous methods of selection were introduced by Rabbethge and Giesecke (1862), who analysed selected beets cut into portions and determined, not only the richness in sugar, but also the purity of the juice polarimetrically. Kuhn then improved the selection still further by microscopic examination of the seeds.

Choice of seed is of great importance and seed should be obtained only from reliable firms; a saving of a few shillings in buying seed sometimes involves serious losses.

Special preparation of the seed (shelling, impregnation, etc.) does not appear to have any practical value, but, on the other hand, Briem (1910) states that repeated selection and adaptation to the new intensive culture methods is able to produce in 20 years an increase in the mean saccharine content from 14 to 19 per cent., besides an increase in the weight of the beets owing to the roots becoming accustomed to more energetic fertilisers.

FIG. 316.

There are now numerous varieties of beetroot known by the names of their producers or of the places where they were first selected. Among such varieties the best are the Klein-Wanzleben, Dippe, Kuhn, Braune, Vilmorin, etc.; these may be distinguished, although not always readily, by the shape of the roots and leaves and by the saccharine content.

Beetroots for fodder or for domestic purposes are yellow or red, but those selected for sugar are white, and any variegation or colouring with the original tint indicates faulty selection and degeneration or reversion to the primitive type. Roots with few leaves or with long stems are poor in sugar, and denote that the soil is of a character not adapted to their cultivation.[1]

The proportions of the principal components of the beetroot vary between the following limits (percentages): water, 75 to 86; sugar, 9 to 18; cellulose and lignin, 0·8 to 2·5; nitrogenous (protein and amino-) substances, 0·8 to 3; fat, 0·2 to 0·5; mineral matter (potassium and other salts), 0·2 to 2. Other and less important components of the beet are: glucose, raffinose, organic acids (oxalic, malic, tartaric, citric, malonic, succinic, glutaric, gluconic, tricarballylic), amido- and amino-compounds (leucine, asparagine, betaine, tyrosine), gums, pectic matters, coniferin, etc.

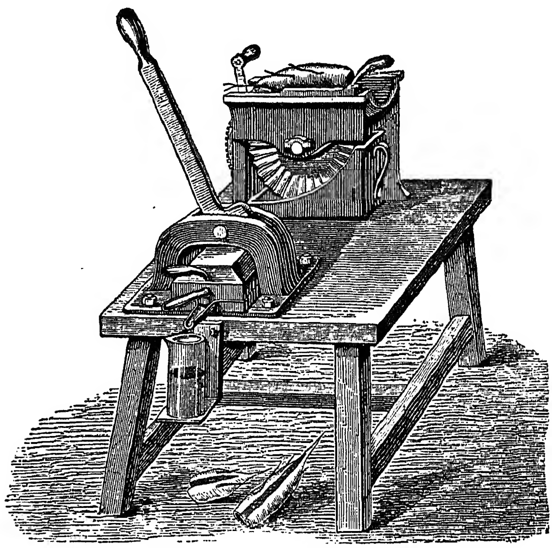

FIG. 317.

The value of the beets was formerly arrived at by measuring the density of the juice with the Brix densimeter, but the results varied considerably with different varieties of beet and also from other causes. It is usual nowadays to determine the quantity of the sugar in the juice by means of the polarimeter (*e.g.*, the Soleil-Ventzke-Scheibler or, better, the three-field instrument of Schmidt and Haensch; *see later*).

[1] **Beet Cultivation.** Sandy or very compact (clayey) soils are not suited to the growing of beet. The most suitable are medium soils which can be worked to a considerable depth (35 cm.) in the *summer* months. In Italy, where the rain is not so well distributed as in Central Europe, it is necessary to sow early in order to avoid the excessively dry season.

Fertilisation should be abundant, since from a hectare of soil beets remove annually as much as 120 kilos of potash (K_2O), 52 of phosphoric anhydride, and 69 of nitrogen. Stable manure serves well as the fundamental fertiliser, but the sugar manufacturers require the farmers to apply it in the summer, during tilling, and not in the spring; any large use of nitrogenous manures is inadvisable. According to Stoklasa (1910), the most suitable manuring for beet is obtained by a rational application of nitragine (*see* Vol. I., p. 349). As supplementary fertilisers, superphosphate (about 4 quintals per hectare) and sodium nitrate (1 to 1·5 quintal per hectare) are largely used. To ascertain if a soil requires also potash (kainit, carnallite, chloride, etc.), the presence or absence of potassium salts in the drainage water is determined by analysis. In general, however, 1·5 to 2 quintals of potash fertiliser are employed per hectare. In all cases these chemical fertilisers should be administered at intervals prior to May, as otherwise the sugar manufacturer may refuse the roots owing to the excessive amount of salts in the juice; not only is the latter rendered more impure, but the salts, especially chlorides, prevent the crystallisation of part of the sugar. Irrigation is inadvisable, and in some cases, is prohibited. A large area of soil in the province of Magdeburg became infertile owing to the repeated cultivation of beet, but it recovered its original fertility after the discovery of the deposits of potassium salts at Stassfurt.

In sowing (which is carried out between the beginning of March and the middle of April, with a drilling machine giving rows 35 to 40 cm. apart), excess of seed is always used, so that after the plants have begun to grow, 15 to 16 per sq. metre may remain. The roots then attain an average weight of 500 to 600 grms. (isolated beets sometimes weigh 4 to 5 kilos) and, under favourable conditions, a hectare yields 300 to 400 quintals of beet (in Ferrarese as much as 600 quintals are obtained, while in the other Italian provinces the average is about 300). If sowing is delayed too long, the roots do not mature well but remain acid and give very impure juice.

Growth begins five or six days after sowing, and when the seedlings are a few centimetres high women and children proceed to thin them out with ordinary hoes, just as is done with maize. Later on, the ground is hoed several times to remove weeds and to keep the soil sweeter in the warm weather.

If the season is a wet one, the roots are late in maturing (end of September or, in Germany

A sample of the beets arriving at the factory is obtained by allowing 50 to fall into a basket while the waggon is being unloaded, placing the 50 in a row and taking the alternate ones, repeating this operation on the 25, and of the 12 thus obtained choosing one small, one medium, and one large. From each of these three, a longitudinal portion is removed by means of the *Pellet rasp*, which gives directly a homogeneous paste, the juice being expressed from this by a hand-press (Fig. 317). Of the well-mixed juice, 26·048 grms. (the normal weight of the polarimeter; *see later*) are introduced into a 100 c.c. measuring flask, which is filled to the extent of about two-thirds with water and 5 c.c. of basic lead acetate solution; after the flask has been well shaken, one or two drops of ether are added to remove the froth, and the solution made up to volume with water, filtered through a dry filter, and read in the polarimeter in a 20 cm. tube (*see later*).

At the same time the Brix densimeter is used to determine the density, so that the quantity of non-saccharine substance (*non-sugar*) and the purity may be estimated. The quotient of purity is obtained by multiplying by 100 the ratio between the true sugar-content and that (greater) indicated by the densimeter.

The sugar may also be determined by direct extraction for 2 hours in a Soxhlet apparatus (*see* p. 462) of 26·048 grms. of the beet pulp, mixed with 3 c.c. of basic lead acetate solution, with 75 c.c. of 90 per cent. alcohol. The alcoholic sugar solution is cooled, made up to 100 c.c. with water, filtered through a dry filter, and polarised in a 20-cm. tube. A very sensitive test for indicating if all the sugar has been extracted from the pulp in the two hours consists in adding to a couple of drops of the last drainings from the Soxhlet apparatus 2 c.c. of water and 5 drops of a fresh 20 per cent. alcoholic α-naphthol solution, and then pouring 10 c.c. of concentrated sulphuric acid (free from nitric acid) carefully down the side of the test-tube; in presence of sugar, a violet ring (not green, yellow, or reddish) forms at the surface of separation of the two liquids (*see also* p. 539).

EXTRACTION OF THE SUGAR FROM THE BEET. After many and varied technical and economic difficulties had been overcome, the beet-sugar industry became firmly established and has during the past 40 years assumed great importance, not only on account of its magnitude, but also owing to its technical perfection, which makes it a model of what a great modern chemical industry should be.[1]

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end of October) and are poor in sugar, and have soft tissues which readily give up their juice. In Italy, harvesting takes place normally in August, or, in some cases, earlier than this.

When the beets are ripe the leaves dry somewhat and, if the roots are not dug immediately, in warm climates new leaves may be formed to the detriment of the sugar-content. On this account the factories are arranged so that they can deal in a short time with the whole of the crop. The harvesting is carried out in several portions, since the manufacturer requires roots not more than 3 to 4 days old, alteration occurring on storing.

Beets which have flowered prematurely (in a cold spring or a very dry season) are hard and difficult to exhaust, and the manufacturer demands that such plants should be pulled up or, at least, that the flowering shoots should be suppressed. Putrefaction of the roots, besides injuring the quality and quantity of the crop, sometimes damages a large part of the beet. Among the various insects injurious to the beet is one which destroys the feeble plants.

In soil which is worked insufficiently and not deep enough, or is treated too late with stable manure, the beets tend to form bifurcated roots and so give an increased amount of waste, which is not paid for by the manufacturer.

The manufacturer usually deducts 5 per cent. or, in exceptional cases, more, on account of admixed stones, soil, etc. As a rule, roots containing less than 9 per cent. of sugar are not accepted.

A few years ago the proposal was made that the dried leaves of the beet should be utilised as fodder, of which Germany alone could produce £8,000,000 worth annually.

[1] **History of the Technical Development of the Beet-sugar Industry.** — In his earliest industrial trials, Achard (1786) extracted the sugar by boiling the beets in water, expressing the juice, concentrating this to a syrupy consistency, and allowing to crystallise in the cold. In France, to facilitate the separation of the juice, the beets were disintegrated by means of rasps which converted them into a fine paste, this being squeezed in screw presses and later in far more powerful hydraulic presses. The juice was then defecated with lime and, after neutralisation with sulphuric acid, concentrated in copper pans. On cooling, crude crystalline sugar was obtained.

In Germany, however, the juice was first treated with sulphuric acid and, after a short rest, neutralised with chalk, heated with lime and filtered. The saccharine solution was concentrated by direct-fire heat and decolorised with animal charcoal, albumin, or even blood. The crystallisation was carried out in wide, shallow pans.

In some places use was made of the old Colonial process of concentrating the juice until, on cooling, it gave a dense mass of crystals which was introduced into inverted conical moulds. The point of the cone was closed by a plug, which was then removed to allow the liquid to flow away, the sugar-loaf being subsequently removed.

We shall now follow shortly the whole of the working of a rational sugar factory as far as the refining of the crude sugar and the utilisation of the molasses.

(1) Storing and Washing of the Beets. When the beets are topped and freed from soil

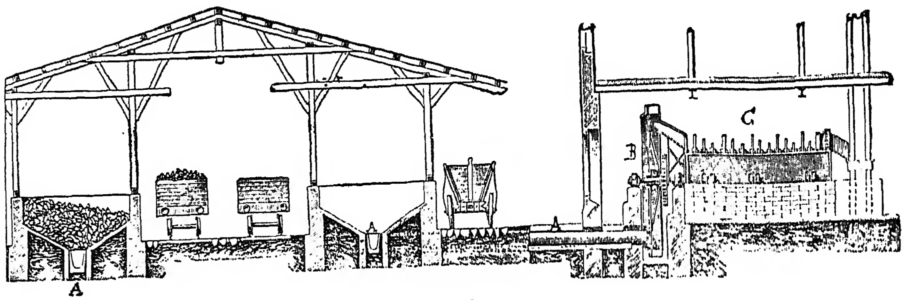

FIG. 318.

and stones they are weighed (1 cu. metre weighs 500 to 600 kilos) and then discharged under long sheds (Fig. 318) with pavements sloping to a longitudinal channel or *flume*, *A*,

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Only later, after a proposal made by Weinrich, was the lime used for defecating the juice neutralised by carbon dioxide instead of by sulphuric acid, inversion of the sugar being avoided and improved defecation obtained. At the outset, the carbon dioxide was prepared by the costly method of treating calcium carbonate with hydrochloric acid, but later it was obtained from the combustion of coal, and finally by heating chalk in suitable retorts or furnaces, the residual lime being also utilisable.

Further improvements were made also in the rasps, as the living cells of the beet, being coated inside with protoplasm impermeable to the cold saccharine liquid, do not allow the sugar to exude; it is hence necessary to rupture the cells as completely as possible.

A considerable advance was made in 1836 by Pelleton, who introduced *cold maceration* of the rasped beet with a counter-current of water. This systematic exhaustion was improved by Schützenbach, who arranged the vessels of beet-pulp in steps, the water entering the top vessel and being collected after it leaves the lowest one and then pumped to the top, and so on; the pulp was exhausted with fresh water and the exhausted pulp replaced by a fresh supply. It was necessary to attend to the cleanliness of the plant in order to avoid the development of micro-organisms capable of inverting the sugar. In 1837 Schützenbach suggested the preliminary drying of the pulp and its extraction with water at 90°, which renders permeable those cells not broken by the rasp. Fesca and Schröttler, on the other hand, centrifuged the fresh pulp directly—just as is now done with the crystallised sugar (*see later*) and subsequently sparged the pulp with cold water in the centrifuge itself so as to obtain more perfect exhaustion, but all these processes were too expensive and did not give complete extraction of the sugar, much of which was still lost.

It was only after 1865, when the *diffusion process* was devised, that complete extraction of the sugar became possible (*see above and later*).

Defecation was also facilitated by separating the organic impurities precipitated by the lime, not with slow and cumbrous bag-filters, but by the filter-press invented by Needham in 1828, improved by Kite and employed in defecating by Danèk in 1862. By this means, working was hastened and cheapened, and further improvement was made when the filter-press was so modified as to permit of the washing and exhaustion of the calcium carbonate with hot water in the press itself.

The application of animal charcoal (bone-black) filters, which had been proposed for other industries by Figuier in 1811, proved of considerable advantage in the clarification and decolorisation. The bone-black readily fixes the colouring-matters and the chalk, but does not retain the sugar. As it becomes enriched in calcium carbonate, however, it loses its decolorising property and hence required frequent renewal at great expense. Subsequently the activity of the charcoal was restored by treatment with dilute hydrochloric acid to eliminate the carbonates and then fermenting at a suitable temperature and with a suitable proportion of moisture, in order to destroy much of the organic matter; the charcoal was then washed thoroughly with water and dried in long iron tubes heated to low redness in a furnace (*see later*). A factory with a capacity of 4000 quintals of beet per day should have at its disposal 6000 quintals of animal black throughout the whole season. The cost of this is considerable, and during recent years these filters are being dispensed with in the sugar factory, methods of defecation being improved and the filters used only in the refinery.

The sugar solutions were, at one time, evaporated by direct-fire heat, a total of 40 kilos of coal being consumed per quintal of beets. In 1828, Moulfarine and Decquer in France introduced the use of steam-coils, and in 1840 the employment of the Hovard vacuum evaporator reduced the consumption of coal to 25 kilos. Since 1852, simple or multiple-effect vacuum evaporators (Rillieux) have come into use, and these, after many improvements, have still further diminished the amount of coal required, until nowadays it is only 7 to 8 kilos.

which is covered with movable boards or gratings and has water flowing through it (Fig. 319). The beets should not be kept long in these silos, as after a few days loss of sugar occurs. The sugar-works are, however, designed to deal with a large quantity of beets every day (4000 to 8000 quintals), so that the whole of the year's crop may be worked up in 50 to 60 days. In order to transport the beets to the place where they are first required, the covering of the water-channel is gradually removed so that the roots fall into the water, which carries them half floating to the principal elevator, *B*, this separating the mud and water and delivering the beets to the washer, *C*.

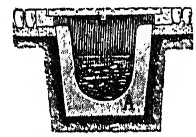

Fig. 319.

The elevator may consist of a large wheel fitted with a number of perforated plates (Fig. 320) or of an inclined screw having a perforated sieve-plate at *G* (Fig. 321).

Nowadays, however, the beets are conveniently raised by applying the principle of the Mammoth pump (*see* Vol. I., p. 303), which also admits of a more complete washing.

The washing is carried out in iron or concrete vessels, 4 to 6 metres long and 1·5 to 2

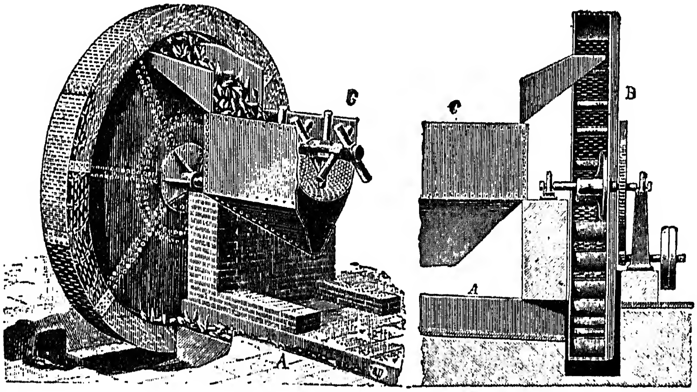

Fig. 320.

metres wide, furnished with a longitudinal bladed spindle by which the roots are beaten in the water and transferred to the other end of the washer; on the bottom are indentations or an inclined plane on which any stones collect, to be discharged from the orifices, *D* and *E* (Fig. 321).

In 24 hours such a washer can treat as many as 500 tons of beet, about 5000 hectolitres of water being consumed.

From the washer the beets fall into basins, whence they are raised by a large vertical elevator to a higher part of the factory and dropped into a double automatic weighing machine, which discharges 50 to 100 kilos or more at a time into the *cutter* or *slicer*; in the latter they are reduced to thin slices suitable for extraction by the diffusion process. The slicing machine is formed of a vertical chamber, *A* (Fig. 322), which receives the roots, and the base of which consists of a circular cast-iron plate, *C*,

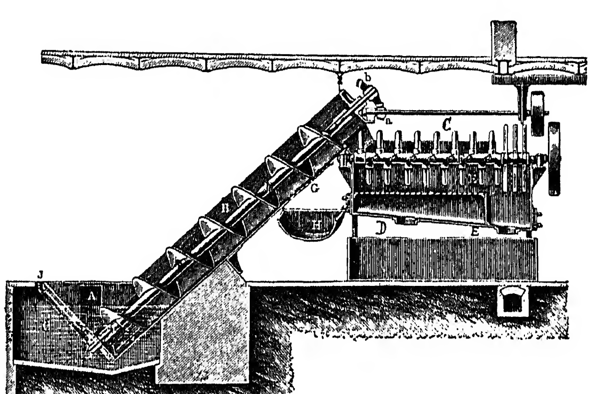

Fig. 321.

rotated by means of a vertical shaft and furnished with 10 to 15 rectangular apertures, *a a* (*see* plan and section, Fig. 323). In these apertures fit cast-iron frames carrying a series of undulating cutting blades which form knives of various shapes (Fig. 324). The beets at

the bottom of the chamber are forced by those above against the rotating knives and so sliced. The form of these slicers varies somewhat in different factories, and in some cases the revolving plate has a diameter of 1·2 to 1·5 metre and a velocity of 100 to 140 turns per minute. The beet-chamber is about 1·5 metre high.

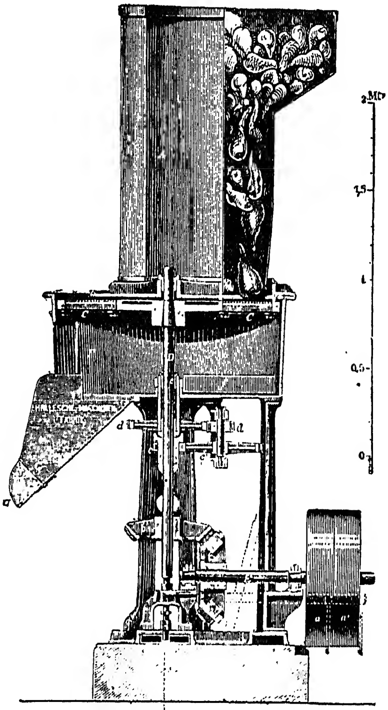

FIG. 322.

At one time use was made of knives with several superposed blades at various distances apart, but these give smooth slices or prisms (if cut longitudinally) which readily adhered one to the other and hence presented a diminished surface in the subsequent diffusion operations. Good results are, however, obtained with those having a zig-zag section (Fig. 325) and giving slices having the form of triangular channels; sometimes a blade is placed at the apex of each angle, so as to prevent the formation of wide slices. The side of the triangle in the blades is 6 to 7 mm., and the thickness of the slices is regulated by the height of the knives above the plate, a (Fig. 324).

Centrifugal slicing machines are also used, these having knives fixed to the inner periphery of the vertical drum, which receives the roots and projects them against the blades. These machines give a greater output and uniform working, the knives being replaceable when in action. The knives usually wear rapidly, especially if stones occur in the interior or in indentations of the roots, and they should be changed frequently, as otherwise they do not cut cleanly but tear, this resulting in slow extraction of the sugar in the diffusors. The knives are sharpened with triangular files or with suitable milling-cutters.

EXTRACTION OF SUGAR BY THE DIFFUSION PROCESS. In the note on p. 545 mention has already been made of the various steps made in the extraction of sugar from beets and of the diffusion process, which is now used and which presents marked advantages over earlier methods. The diffusion process is based on the general laws of osmosis (*see* Vol. I., p. 80). If a solution of sugar (or salt or, in general, any crystalloid) is enclosed in a porous membrane immersed in water, the sugar molecules pass slowly through the membrane to the outside (exosmosis), while water passes from the outside to the inside (endosmosis). This process continues until the specific gravities of the sugar solutions inside and outside are identical (equal numbers of sugar molecules then pass through the membrane outwards and inwards); or, if it is required to remove all the sugar from the inside, the water outside is continually renewed. The same phenomenon is shown by the sugar-containing vegetable cells of the beet. The envelope of the cell functions as an osmotic membrane, although the sugar inside the cell and the walls of the latter also are coated with protoplasm which, at the ordinary temperature, prevents or greatly retards the osmotic flow.

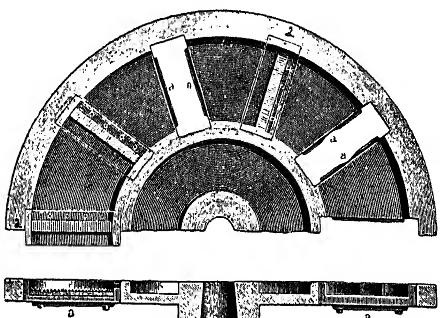

FIG. 323.

At a temperature of 70° osmosis takes place more readily through the saccharine cells of the beet, the protoplasm then coagulating and the walls becoming permeable to the osmotic currents. Under these conditions the complete extraction of the sugar is possible (not more than 0·3 to 0·4 per cent. is left).

The first industrial application of this method was attempted in 1864 by Robert in the

celebrated factory at Seelowitz (Moravia), and the results were so favourable that by 1867 about thirty factories had adopted it. It was soon found, however, that diffusion juices were difficult to filter after defecation with lime, but after Jélinek, in 1865, made use of the filter-presses first shown at the International Exhibition in London, it became possible to

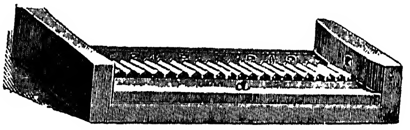

Fig. 324.

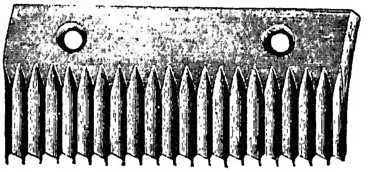

Fig. 325.

defecate even with 2 to 3 per cent. of lime in place of 1 per cent., which was the maximum formerly employable. It was then that the idea was evolved of cutting the beets into slices to facilitate the osmotic phenomena, the extraction being effected by systematic and continuous exhaustion in a series of cylindrical vessels containing the slices. Water at 70° enters the first cylinder, carries away part of the sugar, and then passes to the other cylinders in succession, until it reaches in the last the same density (about 10 to 12 per cent. of sugar) as the saccharine juice of the cells of the fresh beet. When the first cylinder is exhausted it is recharged with fresh slices and placed at the other end of the series. What was previously the second cylinder now receives the pure water and is hence exhausted, after which it is filled with fresh slices and made the last of the battery, and so on. In such manner the process becomes systematic and continuous, being carried on day and night during the whole of the campaign. The circulating water is brought to a temperature of 70° while passing from each cylinder to the next.

Diffusor Batteries. The diffusors are vertical iron cylinders with a capacity of 40 to 70 hectols. and a height double the diameter. They are furnished with an upper aperture

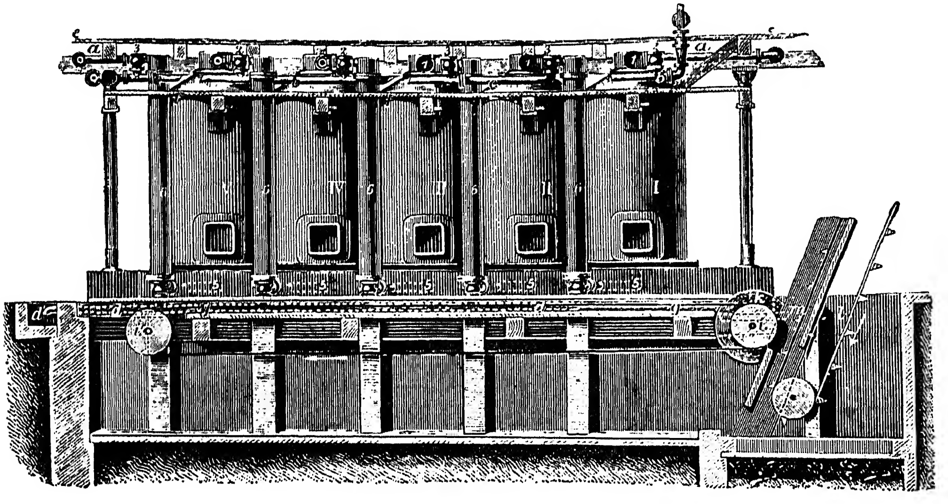

Fig. 326.

for charging with the slices and one at the bottom or side for the discharge of the exhausted pulp.

They are arranged in batteries of 12 to 24 diffusors connected by pipes and valves, heating tubes being placed between. For a factory treating P tons of beet per 24 hours, diffusors having capacities of $\frac{P}{10}$ hectols. each are now used.

The diffusors are often arranged in two parallel rows (Figs. 326, 327, 328), and if they are then discharged laterally the exhausted slices can be collected by means of a single

screw or travelling band, *h*, which carries them to the elevators, *m*; where they are discharged through an aperture in the base (Fig. 329), two channels with screws are used.

Sometimes the diffusors are placed in a ring, as is shown in section in Fig. 330 and in plan in Fig. 331. The diffusors are charged by means either of suspended tubs coming from the slicing machine, or of an endless belt moving above them on rollers and flanked with a fixed plate forming an edge fitted with doors corresponding with the various diffusors. By opening a door and placing a plate diagonally on the belt, the slices are forced off the latter into a sloping channel and so into the diffusor; this operation is repeated until all the diffusors are full.

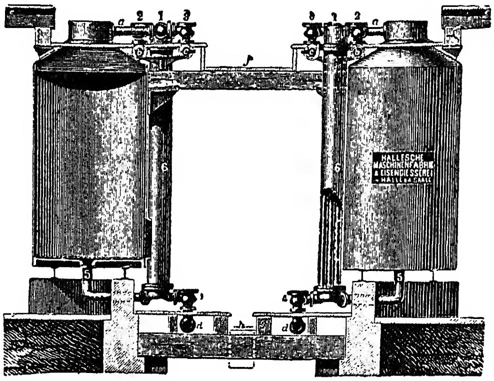

FIG. 327.

When the diffusors are arranged in a circular battery, the slicing machine (*D*, Fig. 330) is placed so that it commands the diffusors, which are charged by means of a shoot, *E*.

A perforated false bottom and an upper perforated disc in each diffusor prevent the penetration of the beet slices into the tubes that supply water or carry off the juice. To avoid accidents when operations are started, the tubes are provided with safety-valves. Air-cocks on the covers allow of the escape of the air displaced by the water entering the diffusors. Thermometers are inserted in the tubes to indicate the temperature of the water and of the circulating juice. There are tubes for cold water, transference of the juice, washing water, discharge of the water, steam for the heaters, and discharge of the juice.

The *heaters* used to regulate the temperature of the circulating juices consist of a series of steam-pipes (*see* 6, Fig. 327) round which the juice passes. A less rational method of raising the temperature consists in blowing steam into the juice; this not only dilutes the juice but may cause caramelisation.

Water is supplied to the diffusor battery through two pipes which join just before the

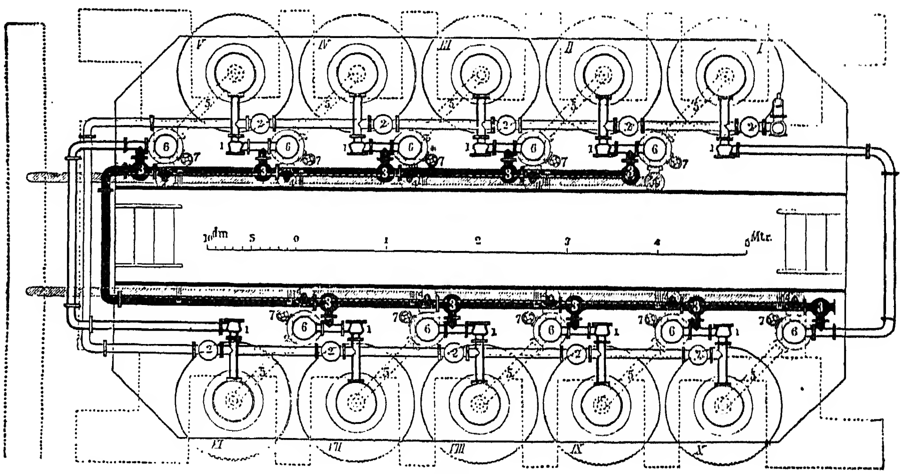

FIG. 328.

diffusor is reached; one of these comes from a cold-water cistern 8 to 10 metres above the level of the diffusors and the other from the boiler. Mixture of the hot and cold water in the proper proportions gives the temperature required for diffusion, this being at first about 35° and later 70° to 75°, to which it is brought by the heaters. Fig. 332 represents diagrammatically the arrangement of a series of diffusors: I to VII, with the heaters

between them; a_1 to a_7, are the air-cocks. The juice-pipe is shown at the top, and b_1 to b_7, c_1 to c_7, and d_1 to d_7, denote valves.

The amount of juice extracted normally by every diffusor is about 48 to 55 litres per hectolitre capacity of the diffusor (*i.e.*, 100 to 110 per cent. of the weight of the beets, since each hectolitre holds 50 to 60 kilos of slices). The amount of water necessary for complete diffusion (including washing water) is 1·2 to 1·5 times the weight of the beet (hence the water-tank should have a capacity at least as great as three or four of the diffusors). In many factories the press waters from the exhausted slices are now recovered (Claassen process), and, together with that from the final diffusor, allowed to settle and afterwards roughly filtered, care being taken that they do not ferment. This procedure is advantageous where introduction of these waters into public waterways is forbidden.

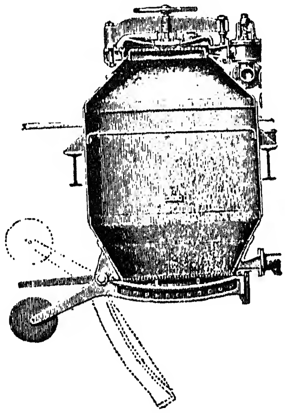

FIG. 329.

Pressing and Drying the Pulp. The pulp (exhausted slices containing less than 0·5 per cent. of sugar) discharged from the diffusors is transported by a screw or endless band to an elevator which discharges it into the *pulp-press* (*B*, Fig. 333), where the water it contains (95 per cent.) is removed as completely as possible. Presses of various forms are used for this purpose.

That of the Klusemann type consists of a vertical, revolving cone of perforated sheet-metal, *C* (Figs. 333, 334), fitted with oblique vanes and enclosed in a stationary cylinder, also perforated. The vanes, which are arranged helically along the cone, compress the mass of pulp against the perforated cylinder and gradually move it downwards

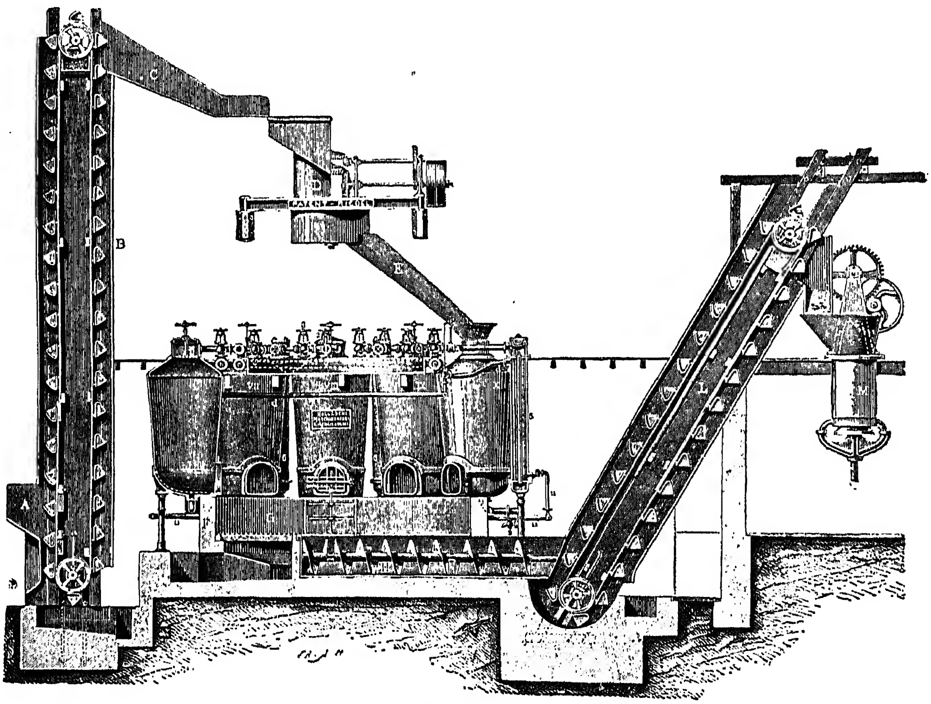

FIG. 330.

where the space becomes narrower, so that a considerable part of the water is squeezed out through the cone and cylinder, which are enclosed in a jacket, *E*; all the water is carried off by the tubes *F*, *G*, and *H*, while the pressed pulp is discharged through the annular orifice, *I*. An arrangement similar to this has also been combined with the pulp-

elevator, which consists of an inclined screw, the pulp being thus raised and pressed at the same time.

The Klusemann press has been improved by Bergreen and others in order to obtain pulp containing much less water and from 14 to 18 per cent. of solid matter. Each 100 kilos of beet yields about 80 kilos of pressed pulp containing, on an average, 85 per cent.

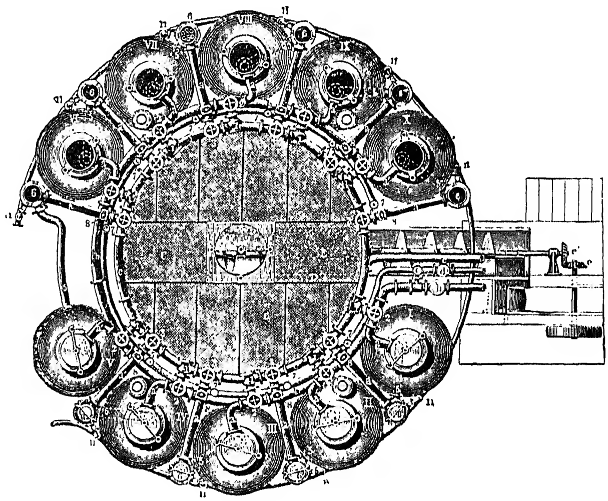

FIG. 331.

of water, 1·5 per cent. of ash, 1·2 per cent. of protein, 0·27 per cent. of fat, 3·5 per cent. of cellulose, and 8 per cent. of non-nitrogenous extractive matter (0·5 per cent. being sugar).

The pressed pulp is loaded directly on the farmers' waggons to be used as fodder, about 8*s.* per ton being paid for it (pre-war); but part of it (30 per cent. of the amount of beets they supply to the factory) is given to them free of cost. If the pulp cannot be sold immediately, it is stored in silos until sold, but if this is done, it readily undergoes putrefactive fermentation, the gasogenic bacteria of which contaminate milk and cause inflation of cheese, so that in some countries an addition of pure lactic acid organisms is made, these

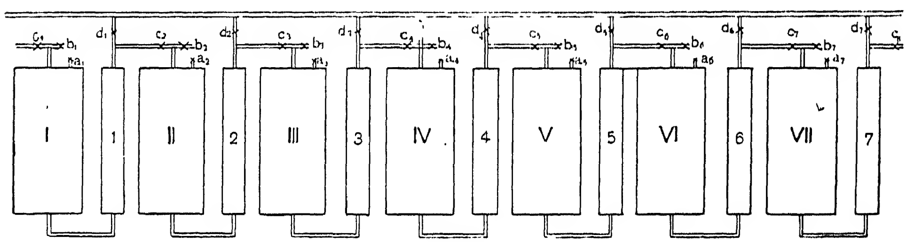

FIG. 332.

preventing other secondary fermentations and enhancing the digestibility. Where fuel is not expensive, it is preferred to dry the pulp at once. It is known, too, that fresh pulp in silos loses as much as 30 per cent. of its solid matter, which is rendered soluble and volatile by bacteria, the sugar being converted almost completely into lactic acid. Furnace gases are sometimes used to dry the pulp.

Of the various types of apparatus for drying the pulp, that of Büttner and Meyer (*see* Fig. 335), which was devised in 1887–1888 and rapidly came into use in Germany, France, Belgium, and Austria, gives good results. In 1898 sixty German factories were employing pulp-driers on this plan. The moist pulp is raised by means of an elevator, *p*, and dropped at *f* into an upper chamber, *B*, composed of four semi-cylindrical channels containing mixers revolving in opposite senses which stir and lift the pulp and at the same time transport it to the mixers of the similar chamber below; thence it passes to a third chamber. A current of air at 400° from a furnace enters *A* at *f* and is moved in the same direction as

the pulp by the aspirator, *C*, which then forces it into the dust chamber, *D*, and thence to the shaft. The pulp should issue at a temperature of 110° so that moisture may not condense on it, and the supply of pulp is regulated so that the final proportion of water present is 12 to 14 per cent.

The composition of the *dry pulp* is as follows: 12 per cent. of water, 6·5 per cent. of ash, 8 per cent. of protein, 1·2 per cent. of fat, 18 per cent. of cellulose, and 55 per cent. of

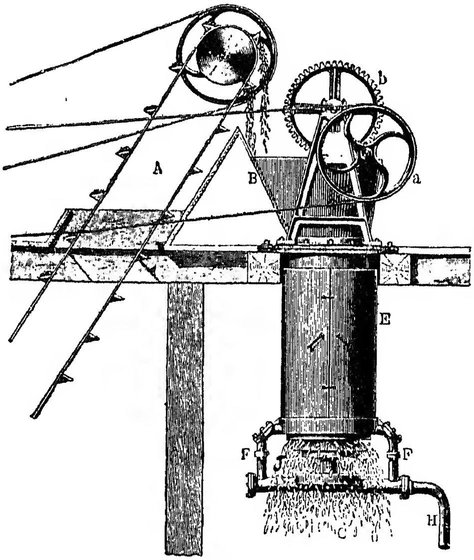

FIG. 333.

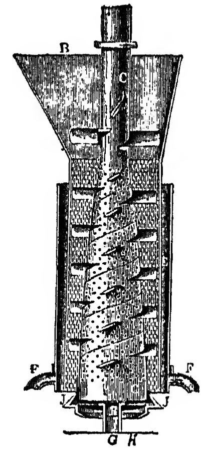

FIG. 334.

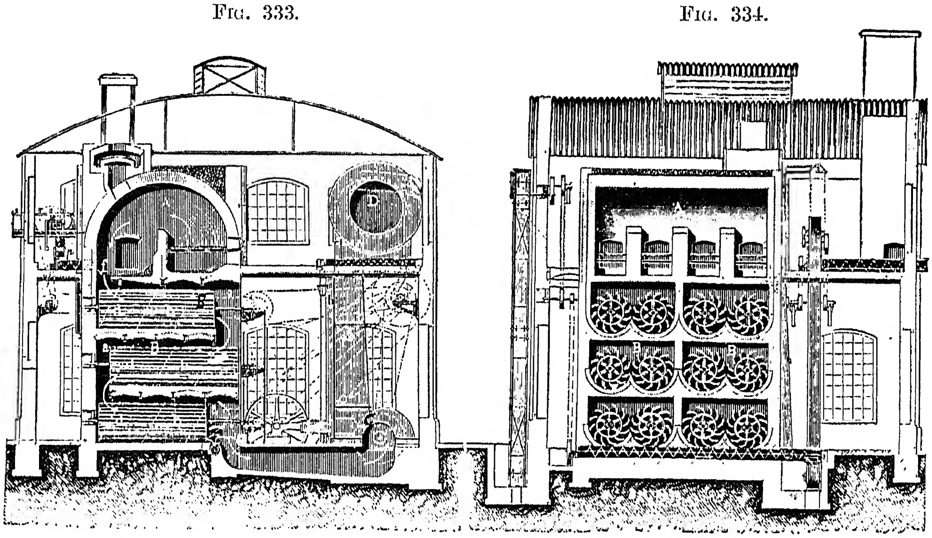

FIG. 335.

non-nitrogenous extractive substances (5 to 7 per cent. being sugar). Tests made by Gorini (1911) show that the dry pulp is not sterile, and may hence be harmful to milk.

THE STEFFEN PROCESS. Some years ago Carl Steffen patented (Ger. Pat. 149,593) a process of extracting sugar from the beet without the use of diffusion, a process resembling that used by Achard 125 years ago (*see* Note on p. 545). The beet slices (containing 75 to 80 per cent. of water) are pressed, giving a juice of 20° to 25° Brix. The remaining pulp is then heated to 85° with more dilute juice (15° to 17° Brix), which is thus enriched with sugar extracted from the pulp. The latter is compressed in a powerful press in the hot, the residual pulp being rich in sugar and hence of greater value for cattle-food. This

process yields less molasses and more *first-jet* sugar, while it requires less expenditure of water, coal, and labour, and a less expensive plant, than when diffusers are used. For each 100 kilos of beet there are 45 litres of water less to evaporate. The Steffen apparatus is shown diagrammatically in Fig. 336. The beets pass into an ordinary slicer, H, and the slices fall into G and then into a horizontal cylinder, M, containing the juice heated to 95° to 98° (600 litres of this juice and 100 kilos of cold slices give a mixture at 85°). A horizontal screw, Z, transports the slices to T, where they meet a double-jacketed (the inner casing perforated) worm-conveyor, F, which raises them and presses them to some extent, so that the juice runs back into M. At the top of this conveyor they are discharged into a press of the type described on p. 551 (Figs. 333, 334). The expressed juice returns through the tube, V, to M, while the pulp falls into Y and is conveyed to the drying apparatus. In order to maintain the juice at a temperature of 85°, part of it is continually forced by the pump, P, through the tube, X_2, to the sieve, K_2, then to the heater, C_1, and through X_3 to the cylinder, M; if necessary, steam is injected by means of the injector, C_2. In order to dilute the juice in M so as to keep it always at 15° to 16° Brix, dilute sugar solution from the washing of the defecation mass in the filter-presses (*see later*) is introduced both directly into the cylinder, M, at R_2 and into the inclined conveyor at R_1. The excess of juice flows continuously through the funnel, A, to the sieve, K_1, which retains finely divided pulp, and then through the tube, X_1, to the defecation apparatus.

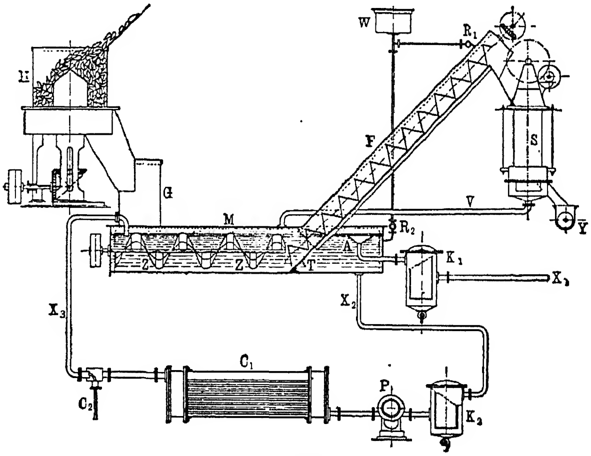

FIG. 336.

This process admits of the rapid treatment of large masses of material, which is heated to 85° in 2 to 3 minutes and yields 70 to 80 per cent. of juice purer than diffusion juice and about 30 per cent. of pulp (containing 70 per cent. of water and 10 per cent. of sugar), which, after drying, contains 10 per cent. of water, 7·6 per cent. of proteins, 0·4 per cent. of fat, 10 per cent. of cellulose, 36 per cent. of non-nitrogenous extractive matters, 52 per cent. of sugar, and 4 per cent. of ash; the expense of drying in Germany is about 6·5*d*. per 100 kilos of the dry pulp.

The diminution of 2 to 2·5 per cent. in the yield of commercial sugar is compensated in various ways; the dry pulp is worth about three times as much as diffusion pulp and before the War was sold in Germany at £5 10*s*. per quintal, in addition to which the diffusion process leads to various small absolute losses.

It must be admitted that, after many trials and much discussion, during recent years, the most competent technical opinion varies with regard to the advantages claimed by the Steffen process. It can, however, be stated that only the most efficient diffusion plant can compete with the Steffen process, which up to the present has been found most advantageous in districts and in seasons in which prices for the dried saccharine pulp are more favourable than those of raw sugar.

In 1910 a dozen factories in Germany alone produced 130,000 tons of sugar by the Steffen process.

In a new process devised by Claassen, all the water from the diffusion of the molasses and that resulting from the pressing of the exhausted pulp are used directly for the extraction of the sliced beets in the diffusors. In this manner all the soluble substances of the beet are returned and utilised, so that an increased yield of sugar is obtained with a diminished consumption of water. This process requires, however, much supervision and care.

The new process devised by Hýroš and Rak employs more perfect machinery than the

Steffen process, yet is identical with the latter in many points; the heating to 85° is, however, carried out in three stages and the final pulp is not dried. This process has been little used, but, according to Herzfeld, could be combined advantageously with the Steffen process.

Other processes, such as those of Bosse, Naudet, Garez, etc., are concerned mainly with the rapid heating of the slices below the slicing machine, pressure or diffusion then being employed.

Juice Measurers. These are special automatic apparatus used to measure the juice extracted at intervals from the diffusors, each such quantity of juice being registered automatically on a strip of paper together with the time elapsing between one discharge and the next. This paper serves to control the working, while it also indicates any stoppages taking place. The underlying principle of such apparatus is the same as that on which alcohol meters (*see* p. 173) are based.

The juice is then discharged through coarse filters to remove vegetable fibres, which are eventually rejected; its concentration is 13° to 15° Balling (11 to 13 per cent. of sugar) and its colour dark brown, and it is subjected to further treatment to prevent its alteration.

This dilute juice is turbid owing to the presence of pectic substances and other suspended impurities, and tends to undergo acid or alcoholic fermentation, as it contains spores which have withstood the temperature of the diffusors. The pectic matters ferment, yielding two mucilaginous acids (Pectic acid, $C_{32}H_{44}O_{30}$, and Pectosinic acid, $C_{32}H_{46}O_{31}$) which render the juice highly viscous and partially invert the sugar. The juice contains also potassium quadrantoxalate and minimum proportions of invert sugar, citric and malic acids, cholesterol, resin, coniferin (which may undergo hydrolysis yielding coniferyl alcohol and then, by oxidation, vanillin; the latter sometimes flavours the raw sugar slightly), catechol, glutamine, betaine, allantoin, and lecithin. Decomposition of the inorganic ammonium salts always present and of the glutamine yields ammonia, which is evolved during the concentration of the juices.

DEFECATION WITH LIME. When the fresh juice is treated with lime, if the latter is not in excess, insoluble calcium pectates separate and part of the sugar may form soluble monocalcium sucrate (*see* p. 539), but if excess of lime is present, the juice is liable to lactic and butyric fermentations, with development of unpleasant odours. If the lime is added to the hot juice no fermentation occurs and part of the organic impurities is precipitated, part also being carried down by the calcium carbonate in the subsequent saturation with carbon dioxide. The latter also decomposes the monocalcium sucrate, liberating the sugar. The potassium oxalate is precipitated as calcium oxalate, soluble potash being liberated; the citric and malic acids and various colouring materials are also precipitated. A small portion of the calcium oxalate redissolves in the saccharine juice.

The treatment of the juice with lime is carried out at 85° in suitable vessels provided with stirrers. The lime is added in the quantity previously determined in the laboratory (2·5 to 3·5 per cent.), and may be as lumps or powder, in which case it heats the juice, or in the form of milk of lime, the concentration of the latter being measured by means of automatic floating densimeters, which give the quantity of lime present. Kowalski and Kosakowski have shown that if, as was long ago recommended, the juice is well agitated during defecation and heating (for 15 to 20 minutes), the total quantity of lime required may be reduced to as little as 1·5 per cent. The lime in the juice is estimated by means of soap solution (Pellet's method) in a way similar to that used to determine the hardness of water (Vol. I., p. 239).

The defecation is followed immediately by *carbonatation* or *saturation* with carbon dioxide; in some factories the defecation and carbonatation are carried out simultaneously and continuously. The carbonatation is effected at 70° to 75°, since at a lower temperature the monocalcium sucrate forms a voluminous double salt rendering filtration difficult.

The operation of saturation with carbon dioxide must be controlled rigorously and continuously in the laboratory, since it is the principal source of loss.[1]

[1] The lime and carbon dioxide used in sugar-works are generally prepared in a vertical lime-furnace (*see also* Vol. I., p. 615), the upper outlet of which communicates with one or two water-cisterns, into which the gas is drawn by an aspirator to be washed and cooled before being conveyed to the saturators. Chalk of good quality (free from iron and containing little sulphate or silica) is used and is mixed with 9 to 10 per cent. of coke (anthracite should be avoided, in order to prevent the presence of odorous and tarry impurities in the gas). The gases contain about 30 per cent. of CO_2, and the size of the suction-pump is calculated on the basis that every quintal of lime produced corresponds with at least 300 cu. metres of gas. The treatment of

In order to avoid the risk of redissolving the calcium carbonate (as bicarbonate), the saturation is first carried on for 20 to 40 minutes at a temperature of nearly 90° until a certain degree of alkalinity remains (0·11 to 0·13 per cent.); the juice is then filtered, heated, saturated again for about 15 minutes until the alkalinity falls to 0·02 to 0·04 and finally filtered a second time. In Austria and Bohemia, however, a little lime (0·5 to 1 per cent., leaving an alkalinity of 0·05 to 0·07 is added before the second saturation in the hot (95°). The juice is then filtered and the third saturation carried out at 100° (10 minutes), the alkalinity being reduced to 0·01 to 0·03. After a fresh filtration, the juice is thoroughly heated for a long time in another boiler, again filtered and despatched to the concentrators. In some factories the third saturation is now made with sulphur dioxide, which has a greater purifying action than carbon dioxide and at the same time decolorises the solution. Liquid sulphur dioxide may be employed, but it is cheaper to produce the gas in furnaces (*see* Vol. I., p. 278). In some works continuous saturation is practised, but without great advantage.

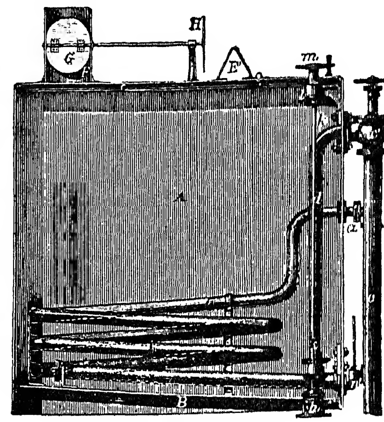

FIG. 337.

The iron saturation vessels (Figs. 337, 338) formerly used were provided at the top with a large tube for the escape of the excess of gas. That used for the first saturation is often 7 metres high, but is filled with juice only to the height of 2 metres (30 to 50 hectols.), the remainder of the space gradually becoming filled with a dense froth; that for the second saturation is 3 metres high, less foam being formed in this case (a large saturation chamber is shown in Fig. 339). If too much froth forms, it can be reduced by the addition of a little coconut oil.

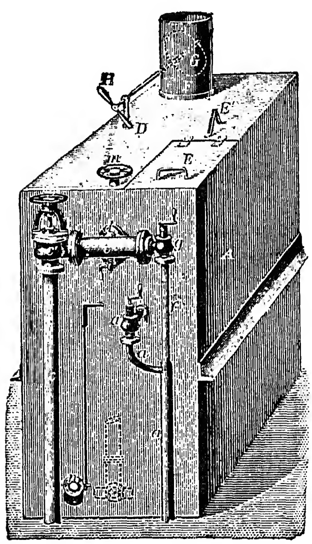

FIG. 338.

The juice is heated for the first saturation by means of a steam-coil, and the carbon dioxide is introduced at the bottom by a perforated tube, *b*. A glass is inserted to permit of the operation being viewed, and a closed orifice, *E*, serves for the inspection and cleaning of the interior.

The completion of saturation is shown by phenolphthalein paper, which ceases to turn violet. Trained workmen also carry out titrations.

A plant for saturation with sulphur dioxide is shown in Fig. 340. The air-pump, *A*, feeds the sulphur furnace, *B*, and the mixture of air and sulphurous acid then passes through the tube, *C*, into the saturator, *D*, the excess issuing by the tubes, *E*.

Behm, Dammeyer, and Schalmeyer propose to purify the juice at 75° with a current of 40 to 50 ampères at 6 to 8 volts for 8 to 10 minutes, using zinc electrodes. This treatment seems to result in the deposition of various organic impurities, but, although promising well, the process has not been adopted.

Filtration of the Defecated, Saturated Juice. The precipitated calcium carbonate is separated by passing the juice through *filter-presses*,[1] which allow the clear sugar-juice to pass through and

5000 quintals of beet per 24 hours requires about 300 quintals of chalk (occupying, in lumps, about 15 cu. metres), which give 170 quintals of quicklime with a consumption of about 85 quintals of coke (9·3 cu. metres in lumps).

[1] **Filter-presses** are formed of a number of iron frames, alternately empty and filled in and supported on two horizontal, parallel rods. An empty frame is shown at *A* (Figs. 341, 342) and a filled-in one at *B* (Figs. 341, 343). The latter is filled in with sheet-iron grooved on both sides, the grooves ending below in two horizontal channels communicating with a single tap, *r* (Fig. 343), or *f* (Fig. 342); the grooves of the two sides are covered with a perforated plate. On the empty frames are stretched cotton or linen cloths, which form two filtering

retain the suspended impurities and the calcium carbonate in the form of cakes, which, after being washed, are readily extracted by unscrewing the press and removing the

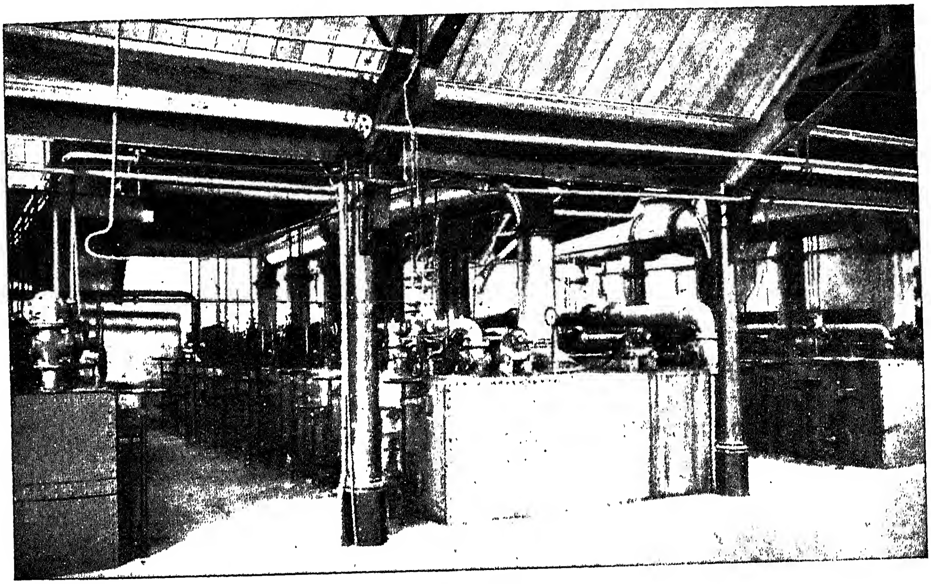

FIG. 339.

frames; they fall into conveyors or trucks underneath, and are often used as lime fertilisers. The first wash-water is added to the filtered juice, while the last is used to slake the lime for defecation.

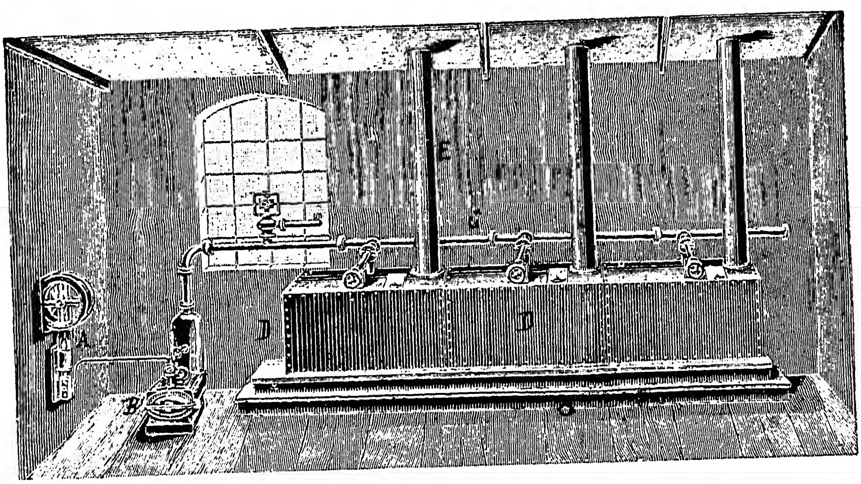

FIG. 340.

The filtering surface of the filter-presses necessary after the first saturation is calculated at 0·5 sq. metre per ton of beet worked in 24 hours; after the second saturation 0·25 sq. metre suffices. The pressed cakes of chalk form 12 to 14 per cent. of the weight of the

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surfaces of the same area as the frame. The frames are squeezed together and against the strengthened block, P, by the screw, V, so that hermetic joints are formed at the edges of all the frames. Each frame is provided with bored projections, a and b, at the top and bottom. When the frames are joined up, the holes in the projections form two continuous channels. The turbid juice enters at a and thence passes through af into all the empty frames, the air being forced out from these through the valve, d. When d is closed, the juice passes under pressure through the cloths on the two sides and the clear liquid flows down the grooves and

beets (*i.e.*, four times the weight of quicklime used). The washing of these cakes require 1 litre of water per kilo.

After the second and third defecations, use is often made, not of filter-presses but of *mechanical filters* (Fig. 345) which also serve for removing suspended matter and residues of the slices from the diffusor-juice.

During the whole of its course from the diffusors and saturators, the juice is under pressure and should rise in temperature from 70° to 100°, but since heat is lost in all the pipes, in order that monocalcium sucrate may not be deposited or the liquor become turbid, the use of *heaters* is necessary for the first and second saturation juices, etc.

These heaters consist of a species of tubular boiler divided into three parts by two plates, *p* (Fig. 346); each of the two end parts is divided into 10 chambers, communicating

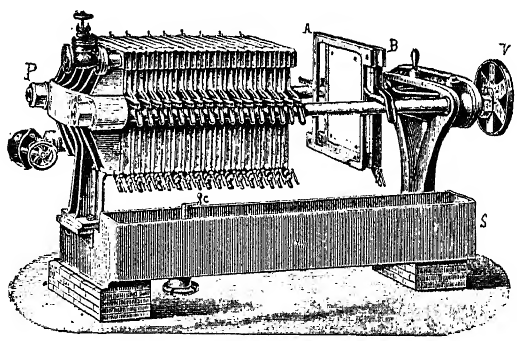

Fig. 341.

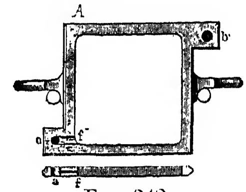

Fig. 342.

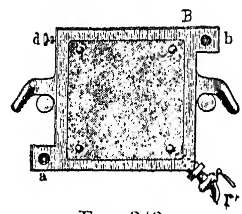

Fig. 343.

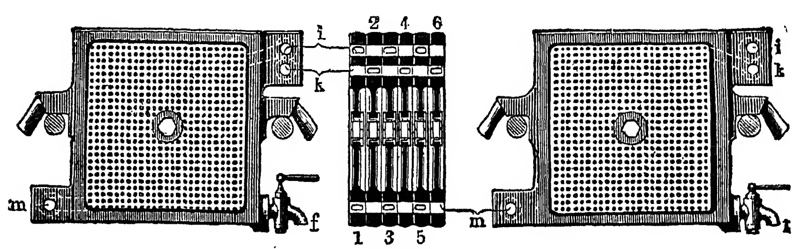

Fig. 344.

in pairs at the two ends alternately. Opposite chambers are connected by groups of long tubes, 4 to 5 cm. in diameter, through which the juice circulates; steam enters at *C*, follows a sinuous path round the partitions, *V*, and finally issues at *D*. The juice enters chamber 1 of compartment I at *A*, and passes through the tubes to chamber 1 of compartment II, then to chamber 2 of compartment II, through the tubes to chamber 2 of compartment I, and so on, until it reaches chamber 10 of compartment I and hence leaves the heater at *B*.

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is discharged at *r* into the tank, *S*. When the frames, *A*, are filled with calcium carbonate, the latter is washed with water to remove the sugar it retains. Since only the alternate grooved plates communicate with the tube, *b*, water introduced under pressure at *b* will pass through the cakes of calcium carbonate in the direction of their thickness and into the grooved plates (not communicating with *b*) to be discharged at the taps *r*. In this way, each cake is brought into thorough contact with the washing water, which can be measured in *S*.

In other filter-presses there are no empty plates (Fig. 344), but each of these has a central aperture over which the filter-cloth, with a hole exactly in the middle, is screwed with a ring from both sides. The juice is introduced into the chambers between adjacent plates, and the wash-water passes under pressure into alternate (odd) plates from the tube, *m*, traversing the cakes, and collects in the other alternate (even) plates which communicate not with *m* but with *k*, the wash-water being thus discharged; the air is initially discharged from the odd frames through *i*. Each press contains 20 to 50 plates, each 3 to 5 cm. thick, and with a length of side 60 to 100 cm. The juice to be filtered is pumped in under a pressure of 3 to 4 atmos.

After the third saturation the juice passes into a final heater or boiler, where it is thoroughly boiled but not under pressure. The juice is moved by means of pumps, a separate one being used after each operation (for raw juice, first saturation juice, second saturation juice, etc.); double-action piston pumps or Girard pumps, with an efficiency of 80 to 85 per cent., are employed.

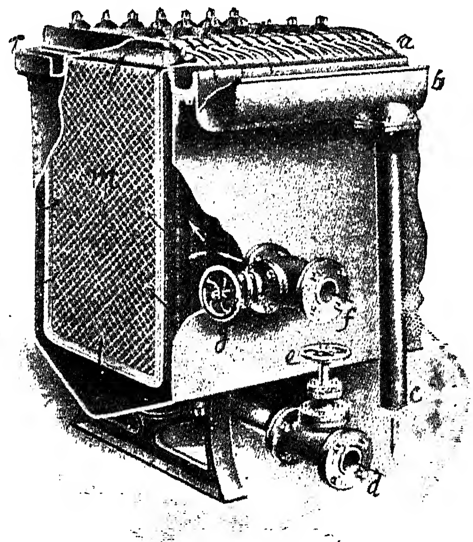


FIG. 345.

When the tax is based on the volume and density of the defecated juice, before the latter goes to the evaporators it passes into tanks under the supervision of the Inland Revenue authorities, who measure the density at 85° to 90° and then reduce it to the normal temperature by means of tables.

CONCENTRATION OF THE JUICE. The defecated, saturated, and filtered juice is pale yellow and perfectly clear; it contains 88 to 90 per cent. of water, 10 to 11 per cent. of sugar, and 0·8 to 1 per cent. of salts. The formation of crystallised sugar requires first considerable *evaporation* or concentration and then *boiling*.

The concentration of the dilute juices is one of the most important problems in sugar factories, the preparation of 74 tons of massecuite containing 7 per cent. of water from 500 tons of beet with a sugar-content of 12 per cent. involving the evaporation of 426 tons of water. Enormous economies are effected by evaporating or concentrating at reduced pressure, which also prevents excessive colouring of the juice, since the boiling-points of liquids are lowered as the pressure is reduced.[1]

[1] The *boiling-point of water* for different degrees of *vacuum* is as follows (Regnault-Claassen): with a vacuum of 50 mm., 98·1°; 100 mm., 96·1°; 150 mm., 94°; 200 mm., 91·7°; 300 mm., 86·5°; 400 mm., 80·4°; 500 mm., 72·5°; 600 mm., 61·6°; 650 mm., 53·6°; 700 mm., 41·7°; 720 mm., 34·2°; 740 mm., 22·4°; 750 mm., 11·8°. It must, however, be remembered that saccharine solutions boil at higher temperatures than water. Thus, under the ordinary pressure, a solution containing 30 per cent. of sugar boils at 100·6°; 60 per cent., 103·1°; 80 per cent., 110·3°; 85 per cent., 115°.

The boiling-point of a liquid for a given degree of vacuum is obtained approximately by *Dühring's law*, according to which the difference between the boiling-points of a liquid at two different pressures bears a constant relation to the corresponding difference for a second liquid. The values of this constant, q, when the second liquid is water are given, for a number of liquids, in the following table, which gives also the boiling-points under various pressures:

Substance	Constant q	Vacuum in millimetres				
		0	526	611	710	750
		Boiling-point				
Water	—	100°	70°	60°	40°	10
Alcohol	0·904	78·26	51·14	42·1	24·02	−3·1
Ether	1·0	34·97	4·97	−5·03	−25·02	−55·03
Acetic acid	1·164	119·7	84·58	73·17	49·84	15
Benzylidene chloride	1·485	210·0	165·5	150·6	120·9	78·4
Benzaldehyde and benzyl chloride	1·353	178·0	133·4	113·9	96·8	56·2
Benzene	1·125	80·36	46·61	35·36	12·86	−20·9
Turpentine	1·329	159·15	119·28	106	79·81	39 54
Butyric acid	1·228	161·70	124·86	111·6	87·02	51·2
Glycerol	1·25	290	252·5	240	215	177·5
Mercury	2	357·25	297·25	277·25	237·25	177·25
β-Naphthol	2	290	230	210	170	110
Phenol	1·2	178	142	130	104	70
Cresol	1·2	190	154	145	118	82

The commonest type of vacuum apparatus with a single vessel or *effet* is the spheroidal form shown in Fig. 347, which is steam-heated and is simple and inexpensive, and is often used in small works dealing with alimentary and other products.

In multiple-effet apparatus the evaporation bodies are simply large wrought or cast

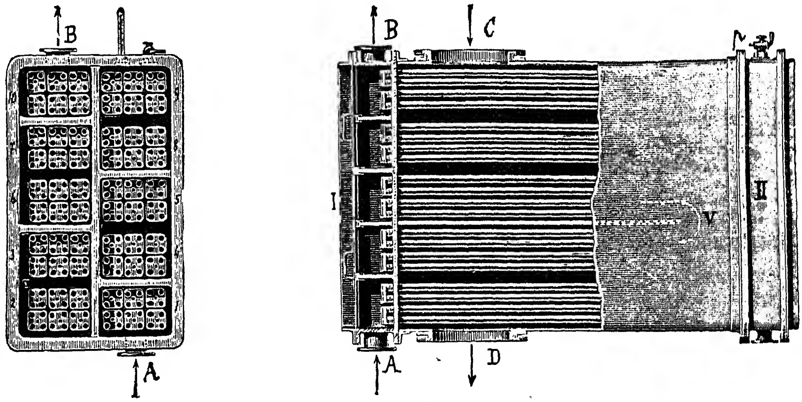


FIG. 346.

iron (formerly copper) boilers surrounded by an insulating earth. These bodies are of various shapes and are placed sometimes vertically and sometimes horizontally. They are usually divided (Fig. 348) into three compartments by means of two partitions, held rigid by a number of brass tubes, 2 to 2·5 cm. in diameter, connecting the first and third compartments. In boilers with horizontal tubes (Figs. 349, 350) the steam circulates in the tubes in a similar manner to the juice in the heater described above (Fig. 346), while the juice surrounds all the tubes. In vertical bodies (Fig. 348) the steam, entering at *A* and issuing at *B*, circulates in the chamber between the two partitions and heats the numerous connecting

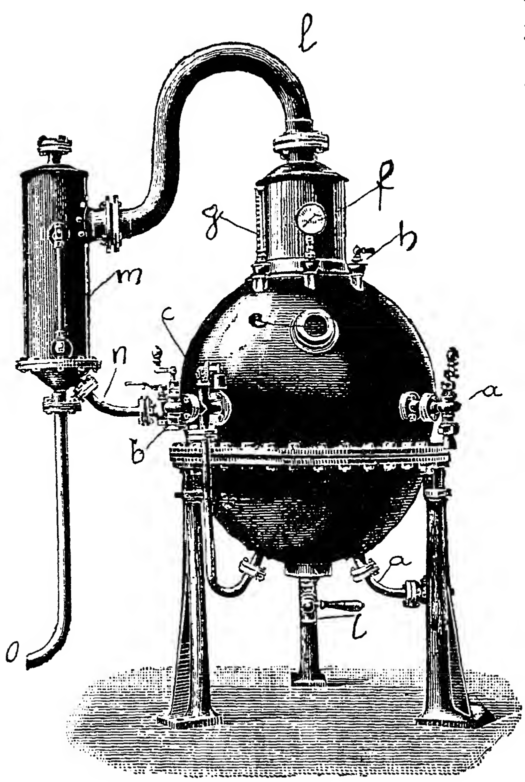


FIG. 347.

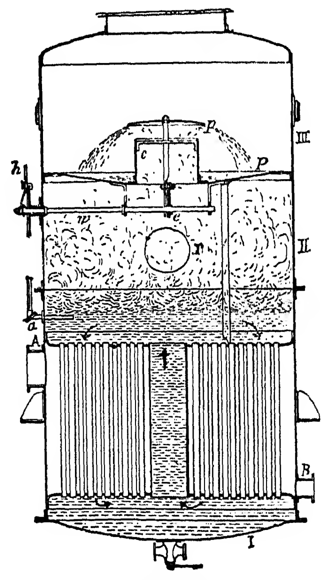
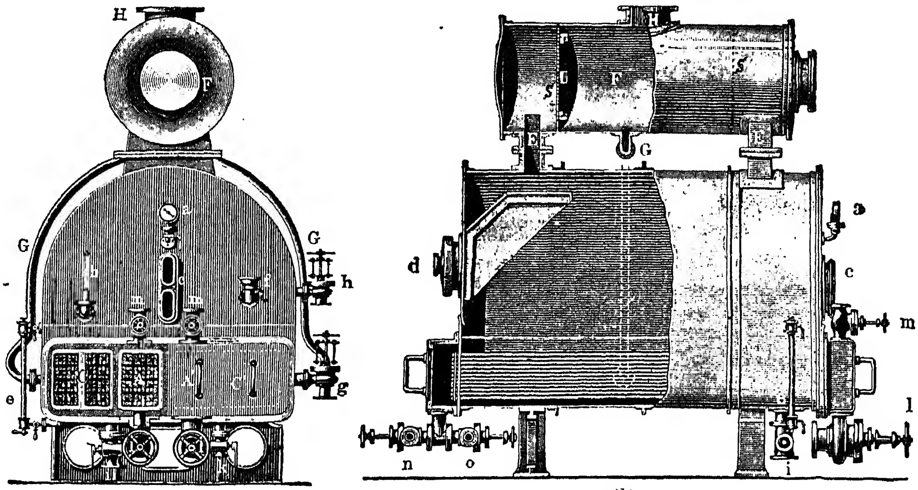


FIG. 348.

tubes. The saccharine solution is thus brought into a condition of vigorous ebullition and circulates rapidly between the lower and upper chambers, as indicated by the arrows in the figure. The level of the liquid, which can always be controlled by the



(a) (b)

Fig. 349.

external glass tube, a, is kept just above the tubes; in this way, less froth is formed, the free vapour space is increased, and danger of caramelisation is avoided. The boiling may be observed through the window, r. In order to separate the drops of liquid carried away in the steam, about two-thirds of the way up the boiler is placed a plate, P, with a large

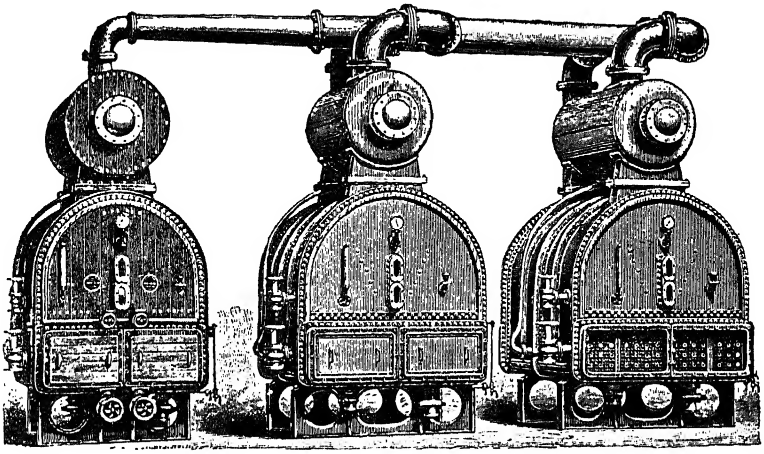


Fig. 350.

central aperture, C, above which is arranged a kind of metal umbrella, p, at a height adjustable by the levers, e, w, and h. This height is chosen so that the liquid condensing above P contains no sugar.

Figs. 349 and 350 show a high-power horizontal evaporator of the Wellner-Jelinek type, and Fig. 351 the arrangement of the pipes therein. The heating tubes occupy only the lower part and are covered by a thin layer of the sugar solution, the steam passing through a long length of tubing.

In a triple-effet plant (as in Fig. 352) the first effet or body on the left is charged with solution previously heated in A and is heated in D by steam at 112° entering the bundle of tubes E at G. The steam from the liquid in the first effet, which boils at 94·6° (vacuum 112 mm.), passes through the wide pipe H and is condensed round the tubes of the second

effet, where the boiling-point is 77·4° (vacuum 442 mm.). The steam from effet 2 passes through *H* to be condensed round the heating tubes of effet 3, which communicates directly by *K* with the barometric columns *LNQ* and by *SR* with the vacuum pump of effet 3 which gives a vacuum of 608 mm. in *F*, the liquid thus boiling at 60°. The pipe, *K*, conveys the steam from effet 3 to the chamber, *L*, furnished with an iron barometer tube, *M*, at least 12 metres long, which dips into a well or water-tank, *T*. The condensation water collects in the tube, *M*, to a height corresponding with the vacuum formed in *L*, and hence in the effet 3, but the majority of the steam condenses in the chamber, *N*, into the top of which the tube, *O*, introduces a fine cold-water spray which produces an abundant and rapid condensation of steam and a considerable lowering of pressure, so that a large quantity of hot water passes into the vessel, *U*, from the barometer tube, *P*. A little steam condenses in the chamber, *Q*, communicating by the tube, *S*, with the suction pump which maintains the vacuum. The vacuum pump may also be connected, by means of three narrow tubes, with the three evaporation bodies, in which the vacuum may be regulated as desired. It is evident that in the three evaporation bodies, especially in *P*, the water must not be kept at too high a temperature, so that it may not evaporate in its turn and may help the condensation of the steam.

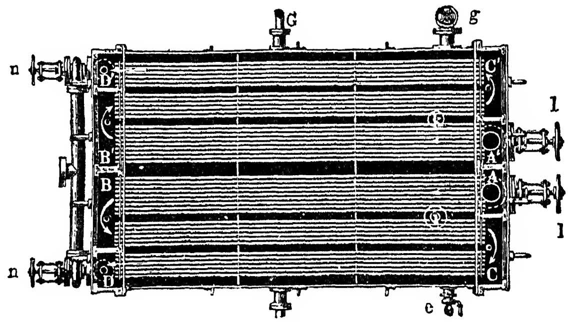


Fig. 351.

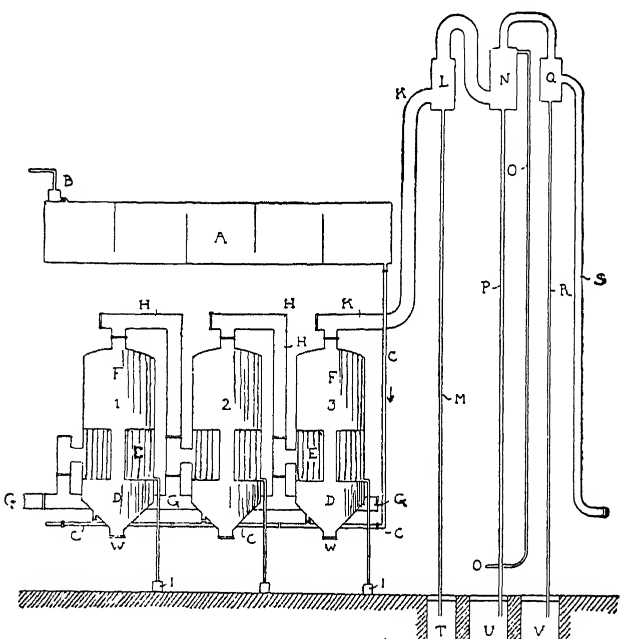


Fig. 352.

In small plants use is made of simple horizontal evaporators with bundles of heating tubes on to which the liquid falls in a thin film in continual circulation, while in Kestner's evaporator the liquid circulates in a thin layer in a system of vertical tubes (*see* Vol. I., p. 563).

In various industries special methods of concentration of solutions are applied, and of these the following may be mentioned.

The solvent may be frozen and removed in the solid condition. Monti (Ger. Pat. 194,235, 1907) suggested the industrial application of this process, which finds a use particularly in the wine industry but is not convenient in the manufacture of sugar.

The Honigmann-Kayser system of evaporation is described in Vol. I. (p. 568).

The auto-condenser evaporator of Prache and Bouillon is based on the principle that, if steam emitted from a boiler at a certain temperature is compressed, its temperature is raised so that it may be used to heat the liquid in the boiler and thus cause continuous evaporation. This evaporator has been developed and has now reached a state of high efficiency.

A somewhat similar method has been applied, in which use is made of a turbo-compressor of the Zoelly type giving an energy efficiency of 60 per cent. or more (Fig. 353). In this apparatus the liquid to be concentrated passes into the vertical boiler and is first heated by live steam circulating round the system of tubes. When the liquid boils the steam is drawn off at the top to the turbo-compressor, which compresses it and forces it round the heating tubes, as shown by the arrow. This compressed steam is condensed and thus evaporates the liquid to be concentrated. Thus the turbo-compressor functions as a thermal pump, transforming mechanical energy into thermal energy. After evaporation has started, very little live steam is required. This system is practicable only when very cheap electrical energy is available. It is not applicable under reduced pressures and cannot be used with liquids giving vapours which attack the metallic parts of the turbo-compressor.

In factories where there is not an abundance of water (that required by vacuum plant is ten to twelves times the quantity of juice to be concentrated), it is convenient to utilise the hot condensed water from the steam-engines (an engine of 350 to 400 h.p. requires about 1 cu. metre of water per minute for condensation) and that from the vacuum concentration batteries. This water is cooled in suitable *atmospheric coolers*, *T* (Fig. 354), so that it can be used in the barometric tubes and also for the washing and hydraulic transport of

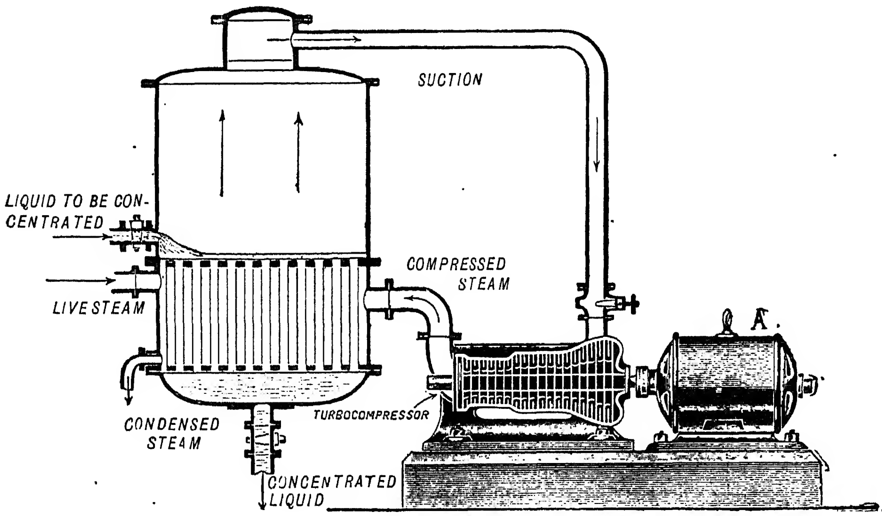


FIG. 353.

the beets. The tank, *K*, corresponds with that marked *U* in Fig. 352. A pump, *A*, forces this water to the top of the pile, *T* (*see also* Vol. I., p. 568), whence it flows down over the faggots built up under a kind of hood, which produces a strong upward draught of air and so evaporates and cools the water (*e.g.*, from 50° to 60° down to 25° to 30°). The latter collects underneath in the tank, *r*, and is then transferred by the pump, *M*, to the chamber, *F*, where the dissolved air is separated and passes out through the pipe, *g* (higher than *G*). The water rises in the tube, *G*, to the top of the barometric condenser, *C*, which is evacuated by the pump, *B*, and the tube, *n*; the pipe, *V* or *S*, corresponds with the tube, *K*, of the preceding figure and communicates with the third evaporation vessel.

Other more efficient arrangements are also used for the cooling of the hot water. Fig. 355 shows a system consisting of numbers of vertical rods arranged in layers crossing one another in a manner similar to those of the apparatus depicted in Figs. 249, 250 (p. 343). The hot water, entering by the pipe, *A*, is distributed homogeneously by means of the tooth-edged channel, *C*, and collects in the vessel, *B*, underneath; the air drawn upwards between the rods carries with it a cloud of steam. Another arrangement is shown in Fig. 356; here a wooden cap or cover fits over walls composed of sticks arranged in the form of venetian blinds, while at the bottom a Körting injector produces a powerful jet of pulverised water in the shape of an inverted cone. The upward air-current evaporates the water while the latter ascends or while it flows down in a thin film on the boards (in this manner only 4 per cent. of the water is lost). Equally ingenious and simple is the

cooling effected by forcing the hot water under pressure into a circular pipe fitted with a number of Körting pulverisers, catching the water in a large tank and, if necessary, passing it again through the pulverisers (Fig. 357); but by this procedure more than 10 per cent. of the water is lost.

In those seasons of the year and on those days when the air is warm and dry, the temperature of the water can generally be reduced to that of the air, but if the air is cold and not very dry, the temperature of the water remains 6° to 7° above that of the atmosphere.

BOILING OF THE CONCENTRATED JUICE. The juice from the evaporators has a density of 28° to 30° Bé (= 50° to 55° Brix) and an intense brown colour, and in order to induce crystallisation of the sugar it is necessary to concentrate it until not more than 15 per cent. of water remains (85° Brix). This concentration or *boiling* is carried out in simple vacuum boilers or *vacuum pans*, the juice being first filtered through mechanical filters, collected in tanks and drawn into the pans which are already evacuated.

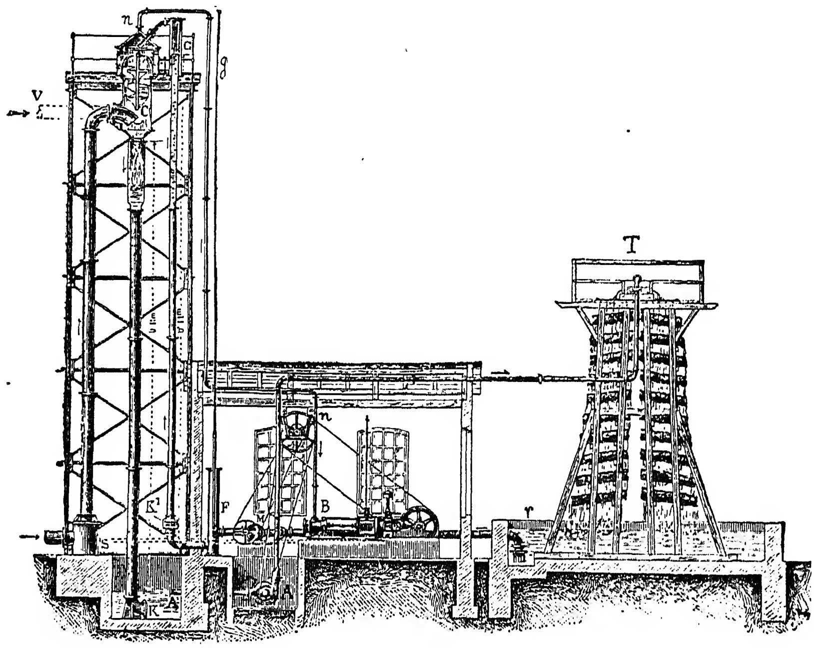


FIG. 354.

These pans resemble ordinary evaporators and are made of sheet-iron; they may be either horizontal (like that shown in Figs. 349 and 350) or vertical. In the lower part of the pan is a dense coil of copper or brass pipes arranged either in a zigzag manner or in concentric circles, and through these passes the steam (Fig. 358); in some cases, however, the bottom of the pan is steam-jacketed (Fig. 359). The concentration or boiling is carried out at as low a temperature as possible and the pan is fitted with a froth-separator (*see* Figs. 348, 349), a tap for the removal of test-samples of the mass towards the end of the operation, and a wide discharge pipe, *K*.

The first thing to be done is to evacuate the pan by connecting it with the condenser and with the vacuum pump. Next the cock of the tube dipping into the concentrated juice tank is opened, the required quantity of juice being allowed to enter. Steam is then passed through the heating tubes. During the boiling, the level of the juice is not allowed to fall beneath the top of the heating tubes, since otherwise sugar would dry on these tubes and be decomposed; so that fresh concentrated juice is introduced from time to time. At a certain stage of the concentration small crystals begin to form and gradually increase in size. The operator extracts samples and spreads them out on glass in order to ascertain the size of the crystals and the density of the mass, and when he considers that sufficient of this *massecuite*—consisting mainly of crystals with a certain amount of dark molasses—has been deposited on the tubes, the heating is stopped and the ordinary pressure estab-

lished in the pan. The whole mass is then discharged from the outlet, *K*, into a large vessel furnished with stirrers, where it is gradually cooled and the crystallisation completed. The boiling and discharging of the massecuite occupy altogether about 10 hours. Fig. 360 shows a battery of Bock cylindrical crystallisers fitted with stirrers.

Larger crystals are obtained by adding to the crystallising vessels a little unboiled juice, which lowers the sugar-content somewhat and retards the crystallisation. When no further

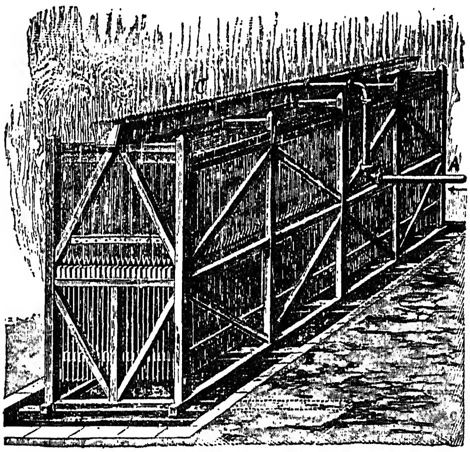


FIG. 355.

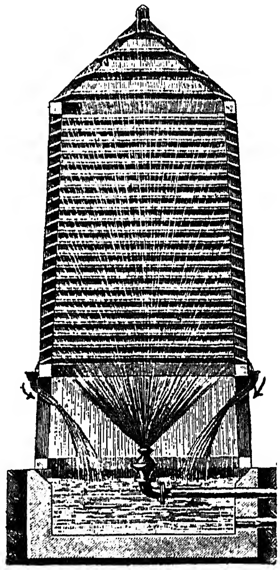


FIG. 356.

crystallisation takes place, the mass is discharged, by means of a parachute at the bottom of the crystalliser, into the centrifuges, which readily separate the liquid molasses from the solid sugar.

This process of boiling is termed *boiling to grain* to distinguish it from the *boiling to thread*, now used only in refining. In the latter case the boiling is not continued until crystals form, the proper density of the boiled juice being ascertained by squeezing a drop between the finger and thumb and then sharply withdrawing the finger; if a filament is

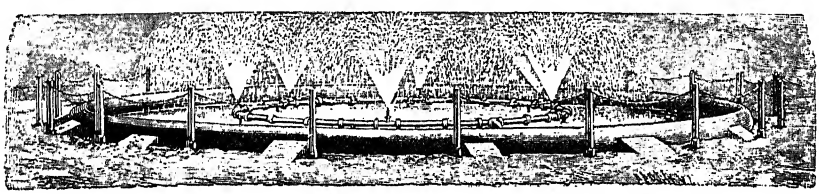


FIG. 357.

thus formed, the boiling is not finished, but the breaking of the thread with formation of two projections indicates the end of the boiling. The syrup is then poured into moulds, which are kept lukewarm until the whole mass sets to an almost solid block composed of finer crystals than in the preceding case.

CENTRIFUGATION OF THE FIRST MASSECUITE. The centrifuges for the *massecuite* have drums of perforated steel with an inner coating of fine-meshed gauze. The diameter of the drum is about 80 to 100 cm., the height 40 to 45 cm., and the speed of rotation 800 to 1000 per minute. The motive force is applied underneath, and the centrifuged sugar remaining in the drum is discharged either above (Fig. 361) or through a door which can be opened in the base of the drum (Fig. 362). The massecuite is passed directly

from the crystallisers to the centrifuges, and, in order to effect more complete separation of the molasses adhering to the surface of the crystals, especially in the layer adjacent to the gauze, so-called *covering* or *clearing* is resorted to ; while the centrifuge is still in motion,

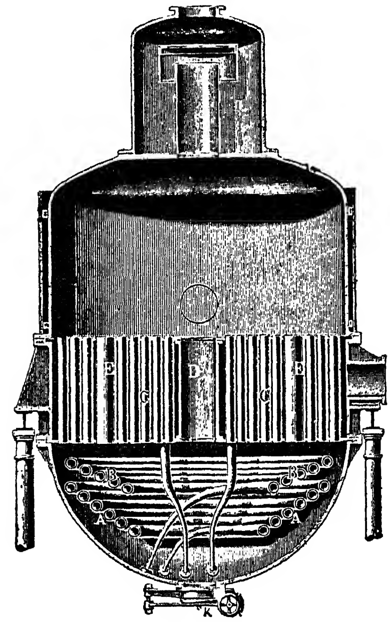


FIG. 358.

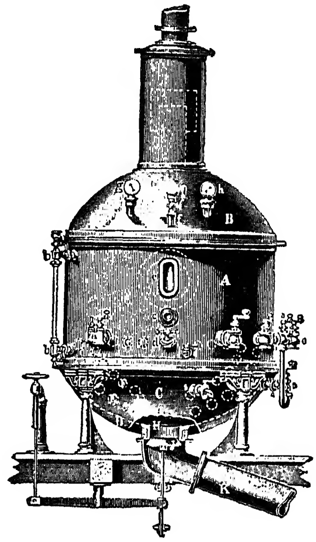


FIG. 359.

sugar is sprayed with finely divided cold or tepid water (Fig. 363), or even with a jet of steam applied inside or, better, to the outside of the basket, the molasses being thereby rendered more liquid. This procedure naturally gives a whiter raw sugar (first product) but in diminished yield, a small part of the sugar being carried away with the molasses by

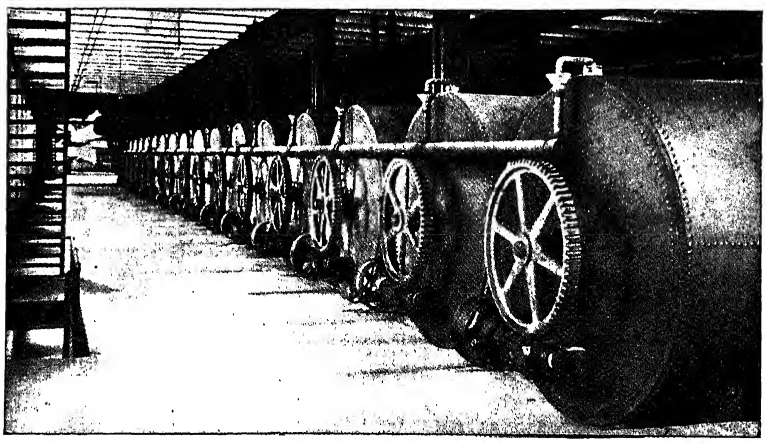


FIG. 360.

the water. This loss is diminished by using, in place of water or steam, sugar juices (syrups) gradually increasing in purity, so that the molasses and less pure syrups are removed and the sugar left covered with a solution of pure sugar. In this way minute, moderately white crystals of sugar are obtained, and these are sometimes placed on the market without refining, but the public suspects them of being adulterated and prefers quite white crystals or cubes.

The molasses from the centrifugation of the first massecuite, after separation of the *first-product sugar* (first runnings), is further concentrated and boiled in *syrup pans*, which are similar to vertical evaporators and are worked under a vacuum, but are usually of single effet. The boiling is continued until the syrup gives a long thread (*see above*), the impurities present preventing boiling to grain.

This *second massecuite* is then placed in large tanks in the *molasses room*, where it is kept for 25 to 30 days at a temperature of 35° to 40°. The blocks of crystals which separate are broken up with suitable bladed machines, and are then delivered to the centrifuges by means of screws or piston pumps. The resulting *second-product sugar* is rather yellow. The molasses which then separates is further concentrated and the third massecuite sent to the molasses room, but no more sugar separates, since the various potassium and other salts present prevent about five times their own weight of sugar from crystallising. This molasses is hence sold as it is for the preparation of cattle-foods or for the manufacture of spirit (*see* p. 166). In some countries, however, it is treated by special processes for the extraction of the sugar still present.[1] Every 100 kilos of beet treated yield 1 to 3 kilos of molasses.

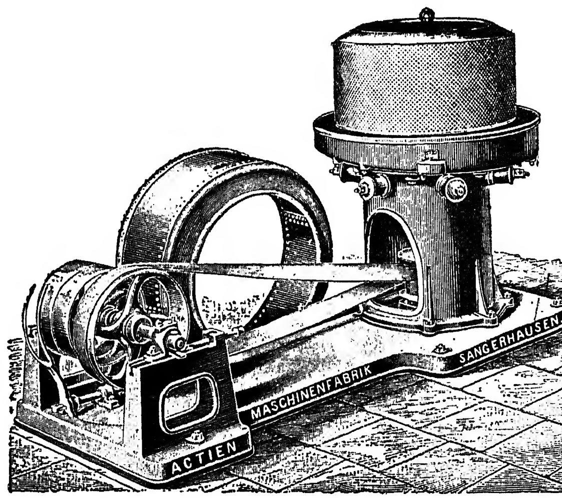


FIG. 361.

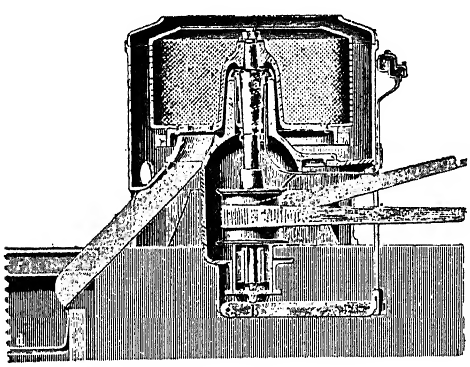


FIG. 362.

The first- and second-product sugars from the centrifuges are sent to the stores, where they are sieved to break up the crusts, which retain molasses. The two products are often mixed, put up in bags holding 100 kilos, and despatched to the refinery.

SUGAR REFINING. The *raw* sugar (*first* and *second products*, with a purity

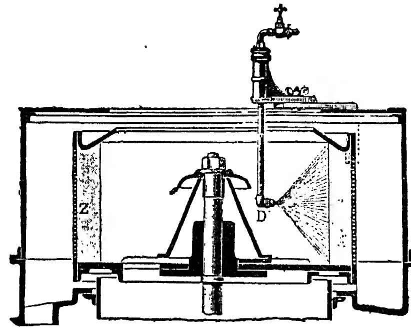


FIG. 363.

[1] In some works the *second product* is obtained much more rapidly by the Bock or the Grosse process. In the first of these, the molasses is not left for 25 to 30 days in the molasses room but is crystallised in 4 to 5 days by continually shaking in large, jacketed drums heated to 90° to 95° and adding a considerable quantity (25 to 30 per cent.) of crystallised sugar. It is then allowed to cool slowly, but at certain times it is heated one or two degrees above the temperatures it shows at those times, so that the smaller crystals formed, and these only, are redissolved. When the mass has been cooled to 35°, the crystalline blocks are crushed and centrifuged, the amount required (25 to 30 per cent.) to induce the molasses (*see above*) to crystallise being previously removed.

In the Grosse process, the mass is kept in motion by a vertical Archimedean screw rotating in the vacuum pan. With this procedure, crystallisation takes place in 48 hours and, after cooling to 40°, the crystalline mass is disintegrated and centrifuged.

Löblich, Zschene, Stenzel, and others have tried mixing the molasses with fresh juice and

of 88 to 96 per cent.) is not usually placed on the market, but is purified in refineries, where it is dissolved in hot water, the purer and less coloured qualities of high *rendement* [1] being kept separate from the more impure grades of low rendement.

The solution, with a density of 37° to 39° Bé., is treated with a little lime, with 3 to 4 per cent. of animal charcoal and often with 2 per cent. of ox-blood, after which it is boiled, the frothy crust forming at the surface being continually broken. The suspended matter is then removed by rapid mechanical filters or by filter-presses. The residue (refinery black) is utilised as a manure, while the hot and still coloured solution is passed through a battery of four or six tower filters, 8 to 9 metres in height and 60 to 80 cm. in diameter, filled with animal charcoal (Fig. 364: *A*, tube for dense juice, *B*, for dilute juice, *C* for water, *D* for steam) and previously heated with steam (*D*) to prevent the sugar separating and to obtain the maximum decolorising action of the charcoal, this being exerted in the hot.

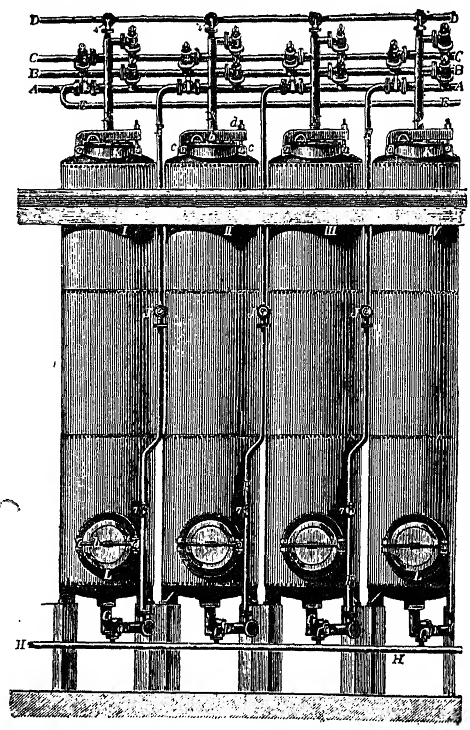


FIG. 364.

The *animal charcoal* or bone-black has a considerable affinity for colouring-matter and for lime, but only a slight one for sugar, but in course of time the pores of the charcoal become obstructed and its decolorising power diminished, so that after a few weeks it becomes necessary to revivify the charcoal.[2]

The solution is passed through the filters in succession and, if necessary, this procedure is repeated. When the syrupy liquid is decolorised, it is concentrated and boiled in ordinary single-effet vacuum pans (of copper) until it shows the grain or short-thread test (*see above*).

When the massecuite reaches this degree of concentration, it is poured into a jacketed copper vessel, in which it is kept at 85° to 90° to initiate the formation of large crystals. It is then allowed to flow into conical copper moulds with their apices, closed by plugs, underneath. The mass, which has just begun to crystallise, is well stirred, and when it has

---

defecating the mixture in the ordinary way, but this process does not seem to offer any great advantage.

[1] The *rendement* expresses the percentage of refined sugar obtainable from the raw sugar and is determined indirectly on the assumption that every 1 part of ash diminishes the refined sugar by 5 parts; thus a raw sugar containing 96 per cent. of pure sugar and 0·4 per cent. of ash would give a rendement of $96 - (0{\cdot}4 \times 5) = 94$ per cent. The rendement is regarded as low if it is less than 94 per cent.

[2] **Revivification of Animal Charcoal.** The charcoal is first treated with hydrochloric acid to remove the calcium carbonate, and if more than 1·5 per cent. of calcium sulphate then remains, this is eliminated by means of hot soda solution. After washing, the wet charcoal is allowed to ferment (first alcoholic fermentation sets in, then acid fermentation and finally putrefaction), and is afterwards washed thoroughly with water, treated with steam, dried and gently ignited in long cast-iron tubes, *C* (Fig. 365), which are heated to about 400° by the gases from the furnace, *A*, access of air to the retorts being excluded. The cooled, free portions are then gradually discharged from the lower parts of the retorts (*E*) into covered metal waggons, so that the charcoal, which is not yet quite cold, may not take fire in the air. The discharge of the putrid washing water from the fermented charcoal into rivers causes serious inconvenience, and nowadays this water is either passed on to the soil or subjected to biological purification (*see* Vol. I., p. 250).

The plant for decolorising with animal charcoal and the revivifying furnaces are very costly, a large amount of the charcoal being required.

Soxhlet avoids the carbon decolorising plant by using filter-presses the chambers of which are filled with a cake composed of wood-meal mixed with various indifferent materials (ground coke or pumice, etc.). By this means sugar solutions can be decolorised moderately well even in the cold.

assumed a certain consistency it is left at rest at a temperature of 35°, so that all the molasses collects at the bottom and can be discharged by removing the plug. In order to remove the molasses completely, the sugar-loaves with their casings are introduced into the moulds of a Fesca centrifuge (Fig. 366), which holds sixteen of them, arranged alter-

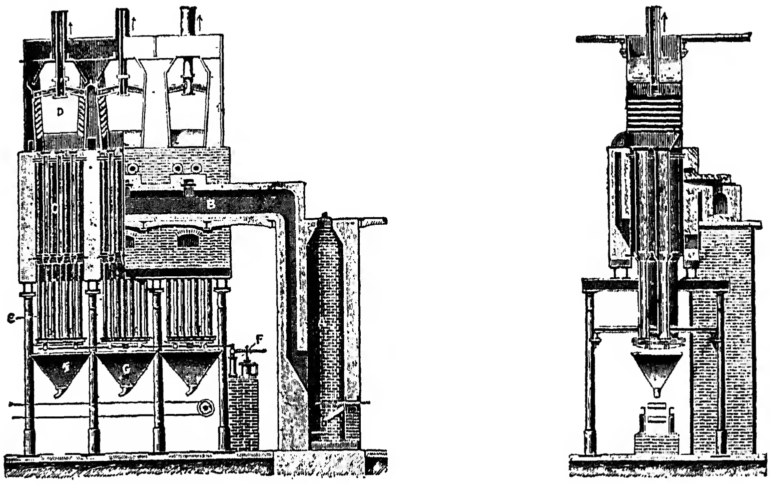


FIG. 365.

nately in two superposed series of eight. The point of the sugar-cone communicates with the aperture, b', of the drum of the centrifuge, and when the latter is charged it is fitted in the middle with a cylinder, $h\ h'\ k$, which rotates with the drum and is provided with channels, S, communicating with all the cones, so that the *covering* solutions (*see above*) may be run in from the tank, r. These solutions consist of three or four pale syrups and three or four concentrated solutions of pure sugar. In order to remove the last traces of yellow colour from the sugar and to blue it slightly, as is sometimes required, the final covering syrup is mixed with a minimum amount of ultramarine (5 grms. per 10 tons of sugar) or methyl or ethyl violet or, better still, according to a recent suggestion, *indanthrene*. The

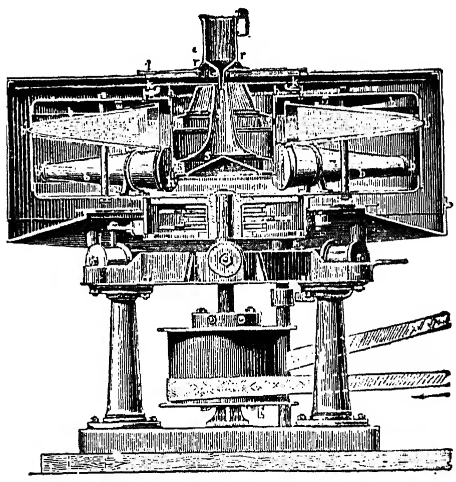


FIG. 366.

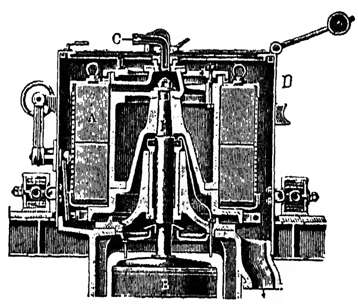


FIG. 367.

white loaves thus obtained are then dried in suitable chambers or in revolving apparatus, at a temperature of 55°.

To obtain white sugar directly, the final massecuite is sometimes decolorised with 30 to 50 grms. of *blankite* per hectolitre (*see* Note, p. 542 ; blankite is pure, crystallised sodium hydrosulphite, the use of which is rapidly extending in sugar-works ; *see* Vol. I., p. 586).

The beet-sugar of commerce should always have a very faint alkaline reaction (towards phenolphthalein), since otherwise it undergoes partial inversion. Cane-sugar, however, has usually a slight acid reaction.

Cube sugar was formerly obtained by sawing the large blocks, this entailing considerable loss, but at the present time suitable centrifuges (Adant type, Figs. 367 and 368) yield directly long rods of sugar of the requisite thickness, these being then sawn with a minimum of loss. A platform, *F*, carries eight vertical prisms, *o*, furnished with screws by which they are fixed to an upper annular disc. The latter is slotted (*c*) to allow of massecuite being introduced into the chambers (*a a*) remaining between each prism and the next, and divided into a number of tall narrow chambers by fixed plates in the grooves, *b*. The platform is introduced into the cylinder, *H*, which fits tightly the periphery of the moulds, these being closed inside by a second cylinder. All the chambers are filled with massecuite introduced through the slots, *c*, the whole being allowed to cool for 12 to 14 hours with occasional shaking. After complete crystallisation, the whole platform is withdrawn by the crane, *G*, and placed in the centrifuge, *D*, which makes about 700 revolutions per minute. The covering is effected at a reduced velocity with sugar solutions entering by the tube, *C*, from a reservoir at a height of 5 metres. After the sticks of sugar have been

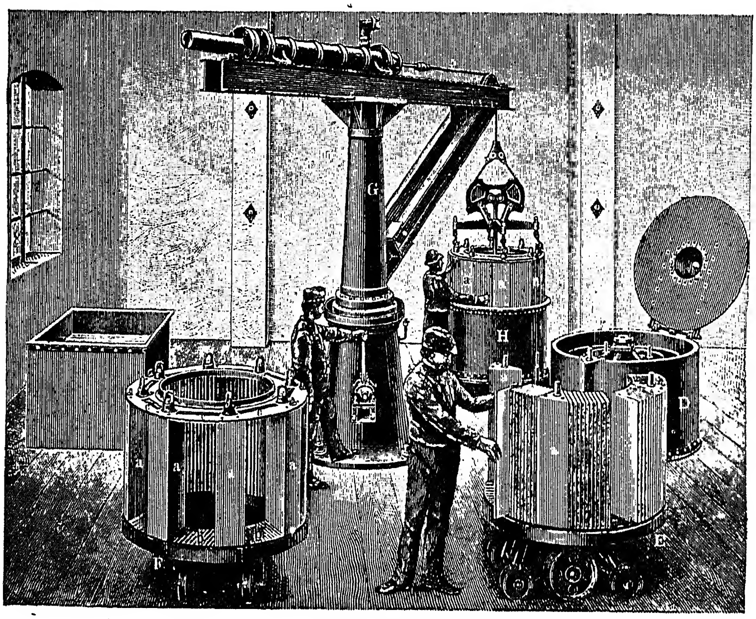


FIG. 368.

removed, the platform and moulds are washed with water and are then ready to receive a fresh quantity of massecuite.

Pilé or *crushed sugar* is obtained in a more simple manner by *covering* the crystalline sugar (from massecuite) in the centrifuge itself by means of water, steam, or pure sugar solution. Slight prolongation of the centrifugation yields a hard, compact mass, which is removed in large blocks and broken into small irregular pieces (pilé sugar) by a special crusher having an indented drum (Fig. 369).

Powdered sugar or *farin* is obtained by grinding lump sugar and any scraps between two smooth, horizontal rollers (*d* and *d'*, Fig. 370) which are brought near to one another by springs and are furnished with scrapers, *f*, to detach the powdered sugar; the latter is subsequently sieved. Powdered sugar can also be obtained by means of the Excelsior mill (*see* Fig. 164, p. 201), which yields as much as 2000 kilos per hour of a sugar not too finely powdered.

UTILISATION OF MOLASSES. The processes employed for the extraction of beet-sugar yield about 3 per cent. (of the weight of beets) of molasses, 2·3 per cent. being obtained in the factories and 0·8 per cent. in the refineries. These are dense, dark-coloured syrups, containing 40 to 50 per cent. of sugar. This does not crystallise owing to the presence in the molasses of 8 to 10 per cent. of mineral salts, which prevent about five times their weight of sugar from crystallising. Hence, in general, it is difficult or almost impossible to

extract sugar by direct crystallisation from syrups with a degree of purity less than 60 to 65 per cent. The percentage composition of molasses varies between the following limits: water, 19 to 28 (mean, 23); sugar, 45 to 54 (mean, 48); *solids not sugar*, 26 to 29 (mean, 28); ash, 6 to 8 (mean, 7; largely potassium salts); invert sugar, 0·1 to 0·4 (mean, 0·15); nitrogen, 1·25 to 1·85 (mean, 1·65). The degree of purity ranges from 62 to 67 per cent. (mean, 64 per cent.). The molasses contains about 10 per cent. of the total sugar of the beet.

The recovery of the sugar from molasses involves indirect processes which are not always convenient in practice, and when this is the case the molasses is employed for the manufacture of cattle-food or spirit (*see* p. 166). In spirit factories the molasses is diluted to 12° to 14° Bé. (about 15 per cent. of sugar), when it can be fermented (*see* p. 166). Ten tons of molasses yield 23 to 25 hectols. of alcohol (calculated as anhydrous spirit) and 1800 kilos of CO_2. The potassium salts are extracted from the residual vinasse by the process described in Vol. I., p. 545. 100 kilos of molasses give 35 kilos of concentrated vinasse (40° Bé.), and by calcining this 10 kilos of *vinasse charcoal* are obtained. In some factories the vinasse is now treated for the recovery of the ammonia and fatty acids by the Effront process described on p. 183, without, however, losing the potassium salts.[1]

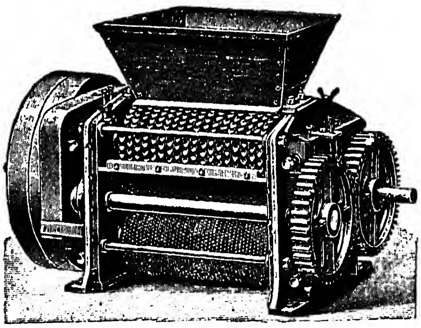


Fig. 369.

In Italy, before the modification of the fiscal regulations which taxed the defecated saccharine juices directly and left untaxed the sugar in the molasses, various factories applied certain of the chemical and physical methods used in other countries for the extraction of the sugar from molasses—by means of osmosis, lime, strontia, baryta (formerly by means of alcohol), etc. When these methods (*see later*) are used, it is calculated that the final molasses does not exceed 0·5 to 1 per cent. of the weight of the original beets.

(1) Osmosis Process. This was first proposed by Dubrunfaut in 1863, and is based on the osmotic properties of crystalloids, which pass through a membrane immersed in water (*see* Vol. I., p. 80). Different crystalloids traverse the

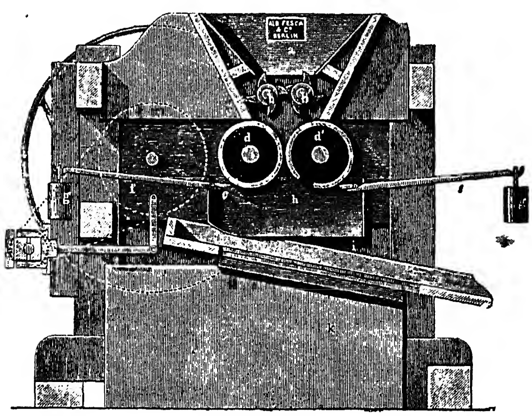


Fig. 370.

[1] The *molasses vinasse* (spent wash) remaining after the distillation of the alcohol has a density of about 4° Bé. and contains 6 to 7 per cent. of solids. When utilised, it is first concentrated to 40° Bé. (100 kilos of molasses give 35 kilos of this concentrated vinasse), when it contains 75 per cent. of solids with about 4 per cent. of nitrogen. About one-half of the solid substances are nitrogenous compounds. The solids contain 10 to 12 per cent. of betaine, 5 to 7 per cent. of glutamic acid, and 1 to 2 per cent. of leucine and isoleucine, besides varying quantities of amino-acids and nuclein bases; the non-nitrogenous constituents consist of about 15 per cent. of fatty acids (formic, acetic, lactic, butyric, and homologous acids), and 15 to 20 per cent. of other organic compounds not completely investigated. Effront thinks it possible, from 10 tons of molasses, to obtain 75 kilos of ammonium sulphate and 95 to 120 kilos of fatty acids, by the action of yeasts which decompose the amino-acids into ammonia and fatty acids, separable by distillation. According to F. Ehrlich, however, yeasts transform amino-acids into alcohol and succinic acid, the formation of ammonia and fatty acids being due not to yeasts but to butyric and other bacteria which always occur with yeasts, and decompose the amino-acids into ammonia, fatty acids, and various amines just as in ordinary putrefaction. Hence the effect of the Effront process could also be obtained by adding to the aqueous vinasse a little putrefied meat and allowing putrefaction to proceed. The manipulation of large masses of putrefied liquid would not, however, be very agreeable or hygienic.

membrane at varying speeds, the sugar, for instance, far more slowly than salts. Hence, if the molasses is placed in a dialyser and surrounded with water, after a time the water will contain more salts than sugar, while the molasses will be diluted with water but will contain relatively more sugar and less salts than at first.

The apparatus now used for osmosis (Fig. 371) consists of a series of wooden frames 4 cm. in thickness and of the size of those used in filter-presses; these are separated by sheets of parchment paper, the whole being pressed tightly together. The compartments thus formed are filled alternately with water and molasses. The upper part of the whole of the osmogen constitutes an open reservoir formed by the upper vertical projections of the frames. The molasses for feeding the alternate chambers is placed in this reservoir and is kept circulating in various ways. The water chambers are fed from the lower part and are discharged through a common upper tube as they become enriched with salts.

The osmotic effects occur best in the hot, so that the molasses is introduced at 80° and the water at 90°.

The taps through which the liquids enter and leave the osmogen are regulated by automatic floats which close or open the taps more or less so as to maintain a constant relation between the density of the exosmosed aqueous solution and that of the osmosed molasses. This relation is determined beforehand in the laboratory, and corresponds with the conditions least favourable to the loss of sugar with the osmosis water and most favourable to the purity of the residual molasses.

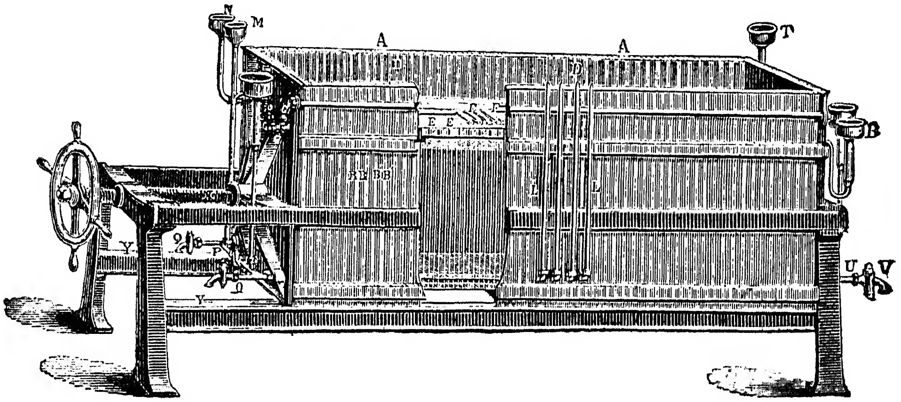


FIG. 371.

The exosmosed water generally has a density of 3° Brix (3 per cent. of sugar and salt together), and the osmosed molasses 35° to 40° Brix (measured at 75° C.); the latter is concentrated and boiled in ordinary syrup pans until it shows the string test. Crystallisation is carried out in the molasses room at 40° to 45° or in the Grosse apparatus. The crystallised sugar is separated by centrifugation and the new molasses obtained again subjected to osmosis. This operation is repeated once or twice more—in fact, until the quantity of sugar extracted would be insufficient to pay the cost. In some cases the osmosis waters are concentrated and reosmosed.

The final molasses and the final osmosis waters—rich in salts and also in sugar—serve for making spirit, shoe-polish, or potassium salts (*see* p. 183). They are also given to cattle, but must then be diluted with solid vegetable products as an excess of salts may exert harmful effects.

(2) **Lime Process.** Steffen found that the addition of finely powdered, sieved quicklime in small portions to a solution of molasses of a suitable concentration (about 12° Brix, *i.e.*, 7 per cent. of sugar, obtained from 1 ton of molasses + 70 hectols. of water), and kept at a temperature below 15°, results in the separation of insoluble sucrate containing rather more lime than tricalcium sucrate, whilst the impurities remain dissolved in the aqueous molasses.

The operation is carried out in a vessel (Figs. 372, 373) similar to the Grosse apparatus, the steam-pipes being used, however, for the circulation of cold water at about 12°, so that after each addition of lime, when the temperature rises 7° to 8°, it can be brought rapidly down below 15°. The addition of lime is continued until all the sugar is precipitated (about

100 kilos of lime per 100 kilos of sugar), this being ascertained by reading the clear liquid in the saccharimeter.

The resultant sludgy mass is filter-pressed at a pressure not exceeding $1\frac{1}{2}$ atmosphere, the filtrate still containing about 0·5 per cent. of sugar, which can be separated as tricalcium sucrate by heating the liquid to 90° and filtering.

The cakes of sucrate are washed several times in the filter-press and the fairly pure residue used to defecate fresh diffusion juice before saturation with carbon dioxide; or the sucrate may be treated with any cold saccharine solution so as to form the soluble monosucrate, the precipitated excess of lime being removed by filtration and the filtrate then saturated with carbon dioxide in the ordinary manner.

(3) **Strontia Process.** When an excess of crystallised strontium hydroxide is added to a dilute sugar solution at a temperature of about 100° and the liquid boiled, a granular,

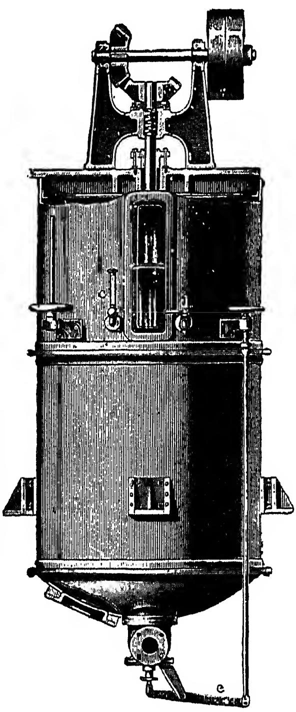


FIG. 372.

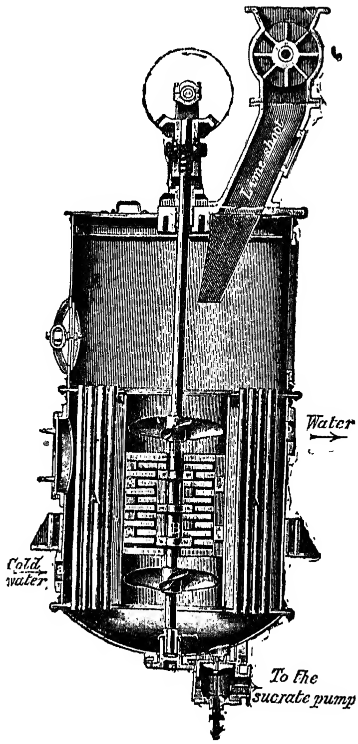


FIG. 373.

sandy precipitate of strontium disucrate is obtained, which is stable in the hot whilst in the cold it decomposes into sugar and strontium hydroxide.

In a suitable boiler provided with steam-coils and stirrers, a 10 per cent. solution of strontium hydroxide is boiled, further quantities of the hydroxide being added until a 20 to 25 per cent. solution is obtained. The molasses is now added in amount equal to about one-third of that of the strontium solution, which is stirred rapidly and heated meanwhile. Strontium hydroxide is subsequently introduced in such amount that the mass has 12 to 13 per cent. of excess alkalinity. The total strontium hydroxide is related to the sugar in the molasses in about the proportion 2·5 : 1.

The precipitated disucrate is filtered rapidly in the hot through bag-filters and washed with boiling 10 per cent. strontium hydroxide, the latter being recovered from the filtrate. The disucrate is then dissolved in a cold strontium hydroxide solution and the solution introduced into metallic vessels situate in an apartment kept below 10°. In the course of three days one-half of the hydrate separates in a crystalline form, the saccharine solution being then decanted and the residue centrifuged. The sugar solution is then saturated with carbon dioxide until it shows an alkalinity of 0·05, all the strontium being thus separated as carbonate. The very pure sugar solution obtained after filtration is concentrated and

boiled as usual, the crystallised sugar obtained being placed directly on the market without being refined.

A somewhat different mode of procedure is that based on the formation of strontium monosucrate, but this does not yield the whole of the sugar as the above process does. In Germany the desaccharification of molasses is effected almost exclusively with strontia in large works specialising in such work.

(4) **Baryta Process.** When solutions of molasses and of barium hydroxide are mixed in the hot in the proportion of 1 mol. of sugar to 1 mol. of the hydroxide, a heavy, sandy precipitate of barium monosucrate is formed which is stable to either hot or cold water; this is collected as usual on filters and freed from impurities by washing with cold water. It is then saturated with carbon dioxide in order to liberate the sugar and, after dilution with other sugar juices, is filtered, concentrated, and crystallised.[1]

YIELD AND COST OF PRODUCTION. Formerly a hectare of land yielded with difficulty 20 tons of beet, but as the result of long-continued improvement of the methods of cultivation, manuring, selection of seed, etc., as much as 30 to 40 tons are now obtained, and in certain special regions (*e.g.*, Ferrarese) as much as 60 to 65.

For every 100 kilos of beet worked, the loss is calculated to be 1·6 kilo of sugar in Italy and only 1 kilo in Germany. The cost of cultivating 1 hectare of beet, including manure, transport, etc., amounted before the war to £12.

Italian manufacturers calculate that in bad seasons the production of 100 kilos of refined sugar required 1 ton of beet, the cost of working this being 7*s.* to 8*s.* (including 3*s.* for coal). Refining cost about 5*s.* 6*d.* (100 kilos of raw sugar give about 90 of refined).

In Germany 100 kilos of beet gave not more than 8·4 of sugar in 1870, about 12·5 in 1890, and 15·8 (including that from the molasses) in 1909–1910. The mean production per hectare was 24 tons of beet in 1871 and 30 in 1910.

The consumption of coal in working 100 kilos of beet in Germany was 35 kilos in 1867, 24 kilos in 1877, 10 kilos in 1890, and 7 kilos (8 in Italy) in 1900. By the use of Kestner concentrators (*see* above) a further saving in coal has since been effected.

The cost of manufacturing 100 kilos of *cane-sugar* in Java varied, before the War, from 12*s.* to 16*s.*, and transport to England or the United States amounted to 2*s.*

STATISTICS.[2] The history of the development of the sugar industry in Europe and

[1] The barium carbonate filtered off is converted into the oxide and then into the hydroxide by heating in suitable high-temperature furnaces.

This barium process was used for some time in Italy, after it had been shown that no danger to health was to be feared from the use of a barium compound, since this is eliminated almost completely by carbon dioxide and the final traces by calcium sulphate. The barium hydroxide required is imported principally from America and Germany, but by 1903, four factories had been erected in Italy for supplying all the baryta necessary to the sugar factories. One of these factories, at Calolzio, starts from barium sulphate; another, at Milan, heats the barium carbonate from the sugar-works; while the remaining two, at Foligno and Pont St. Martin respectively, treat barium carbonate in electric furnaces, making first barium carbide, which with water gives acetylene and barium hydroxide (Garelli's process).

Such treatment of molasses in Italy was found feasible as long as the sugar extracted in this way remained free from taxation, that is, while the tax was levied solely on the defecated diffusion juice. Since 1904, however, the total quantity of sugar produced, including that extracted from molasses, has been liable to duty, and the molasses is consequently utilised in the distillery and in the manufacture of cattle-food. Recently some sugar factories have resorted to treatment of the molasses with barium sulphide, which is much cheaper than the hydroxide and is obtained directly from the sulphate in the electric furnace.

[2] **The Commercial, Customs, and Fiscal Conditions** of the sugar industry in Italy and other countries. In some countries this great industry has been extended artificially owing to the direct and indirect help afforded by the State, and to the speculations of financiers. With the excuse of protecting national industries, Governments have levied heavy Customs duties, with the result that the public has paid dearly for its sugar, while manufacturers have accumulated enormous profits and have been enabled to export sugar at less than cost price to other countries. At first the protective duty was from 24*s.* to 32*s.* per quintal, while in France it was raised to 64*s.* The form taken by the protection was then changed by the institution of export bounties, which allowed the sugar to be sold abroad at a low price, while large profits were made owing to the high prices at home and to the bounties. First Belgium and then France established a bounty of 8*s.* to 10*s.* for every quintal of sugar exported, France being thus subjected to an enormous burden amounting to over £2,000,000, without counting the rebate on the freight from the factory to the frontier. This enormous sum has been paid by the mass of the population, to the exclusive advantage of a few manufacturers (rule of the Méline Ministry).

In Germany and Austria, where the export bounties were relatively low, the manufacturers formed sale syndicates (cartels), which operated in the following manner: the manufacturers pledged themselves to supply all the raw sugar to the refiners, who granted a bounty of 24*s.* per

the importance this industry has assumed during the past quarter of a century have already been discussed on p. 545. Reference has also been made to the production of cane-sugar compared with that of beet-sugar. While in 1854 beet-sugar formed only 14 per cent. of the world's total production (1,423,000 tons), in 1866 the proportion was 30 per cent. (on a total of 2,000,000 tons); in 1878, 44 per cent. (on 3,000,000 tons); in 1887, 47 per cent. (on more than 5,000,000 tons); in 1893, 55 per cent. (on about 6,000,000 tons); in 1899, 64 per cent. (on 7,500,000 tons); in 1901, 67 per cent. on almost 9,000,000 tons. In 1908–1909 cane-sugar again assumed first place, which it has since maintained.

To give an idea of the progress made by the beet-sugar industry during the last 80 years, the production of raw sugar in the two countries where this industry has developed most is given in the following Table:

	In France	In Germany	Germany	
			Yield of sugar per 100 kilos beet	Annual consumption per head
	Tons	Tons		
1840	22,784	14,200	5·9 kilos	2·5 kilos
1850	62,165	53,300	7·3 „	3·1 „
1860	126,480	126,520	8·6 „	4·3 „
1870	282,136	186,000	8·6 „	4·7 „
1890	750,000	1,336,000	12·5 „	8·5 „
1903	1,080,000	1,921,000	14·4 „	13 „
1905	—	1,605,000	14·9 „	14·9 „
1906	730,000	2,400,000	14·7 „	17 „
1909	807,500	2,037,400	16·3 „	19·5 „
1912–13	960,900	2,700,000	16·2 „	21 „
1913–14	738,440	2,478,700	15·7 „	—

quintal to the manufacturer and sold the sugar to the home consumer at a very high price, there being no fear of competition, as they enjoyed a monopoly. The sufferers, as always, were the consumers. The home profits were so enormous that sugar could be sold abroad at less than cost price and competition thus vanquished. On the other hand, England, the greatest consumer of sugar, found its markets deluged with cheap Continental sugar, which competed seriously with that from its Colonies, which had also become considerable exporters.

Under these conditions a more rational solution was found for the problem of sugar with reference to international commerce. The initiation of such an undertaking could come only from England, who was able finally to impose her conditions on all countries sending sugar to her markets. The Brussels Convention, convoked on September 1, 1902, was subscribed to by England, Germany, Austria, France, Belgium, Holland, and Italy. The result was the abolition of export premiums and the reduction of the boundary duty to 5*s.* per quintal above the manufacturing tax, from September 1, 1903, onwards. Such duty was to be enjoyed only by those countries conforming to the Brussels Convention.

Italy did thus conform in a modified way: the boundary duty remained as before, namely, 23*s.* for first quality and 16*s.* 6*d.* for second quality, while a pledge was given not to export sugar to other countries and to impose an exceptionally heavy Customs duty on countries not adhering to the Brussels Convention (especially on Russia and the Argentine Republic; but Russia entered the Convention in January, 1908, and pledged herself to export for six years not more than 200,000 tons per annum of bounty-fed sugar. After 1908 England held herself free to import premiumed sugar without imposing supertaxation). Spain and Sweden were treated like Italy by the Brussels Convention, to which then Luxemburg, Peru, and Switzerland conformed. In Spain an overproduction crisis arose.

In Italy the price of sugar fell, owing to overproduction and frenzied competition, to 92*s.* per quintal, so that in 1901–1903 almost all the sugar factories showed either minimum profits or considerable losses. Indeed, deducting the tax of 56*s.*, there remained 36*s.* as the price of the sugar. According to the manufacturers, 10 quintals of beet, giving 1 of sugar, cost 16*s.*, while the cost of production of crude sugar was 8*s.* (including 4*s.* for coal), that of refining about 6*s.* 4*d.* and that of transport 1*s.* 8*d.*: total, 32*s.* Thus only 4*s.* remained to provide interest on capital as well as depreciation. Hence, in 1904, all the sugar-makers combined to form a syndicate and raise prices, and early in 1905 an increase of 16*s.* (to 108*s.*) per quintal was enforced; with a production of 1,000,000 quintals, this amounted to an annual burden on the consumer of £800,000. Adding to this the protective duty of £1,200,000, it will be seen that, for the luxury of a native sugar industry, the Italians paid an annual tax of £1,200,000 to £2,000,000, the sole gainers being some 30 factories with a capital of about £3,200,000.

The European War brought all these conventions to an end, and in some countries the fiscal regulations have been rendered more severe.

Some of the large factories in France and Belgium have diffusion plants in the middle of the beet-growing districts, the sugar juices after treatment with lime being forced through pipes, often several kilometres long, to the factories, where they are further worked up.

In Germany the beet-sugar industry has reached its greatest perfection and magnitude, and from 1880 to 1902 Germany was the largest exporter (as much as two-thirds of its output). In 1909–1910, in spite of the diminution of exports resulting from the Brussels Convention,[1] Germany exported 423,000 tons of refined sugar and 310,000 tons of the raw product, the home consumption being 1,260,000 tons. The exports were 740,000 tons in 1890, 883,000 in 1904, and 1,145,000 in 1906. In 1908–1909, 358 factories and 39 refineries were working in Germany. Certain German factories, employing 46 workmen, treat 400 to 500 tons of beet, but in Italy many more employees are required. In 1909–1910 Germany produced 10,600,000 tons of beet, but in 1910–1911 only 5,200,000 tons.

In Austria large batteries of diffusors are used and a more complete exhaustion is obtained even at a lower temperature; in general, indeed, the modern plants are more perfect than those in Germany. In 1908 Austria-Hungary exported 610,000 tons of refined and 195,000 of raw sugar.

The following Table shows, for different countries: I, manufacturing tax in pence per kilo; II, retail price in pence per kilo; III, mean annual consumption in kilos per head in 1899, 1909, and 1913; IV, kilos of refined sugar obtained from 100 kilos of beet; V, kilos of refined sugar from 1 hectare: and VI, number of sugar factories.

	I	II	III			IV	V	VI
			1899	1909	1913			
England	0·96	5·3	40	41·1	48	—	—	—
United States	0·96	4·8	28·4	37·2	40	12·44	2706	75
Switzerland	0·67	4·8	25·7	30·2	36	—	—	—
Denmark	0·575	6·7	21·6	35·5	—	13·82	3950	9
Sweden	2·88	7·7	15·7	24·5 / 17·8	—	14·26	3803	21
Germany	1·92	6·2	13·7	19·7	21	16·35	4809	380
Holland	5·47	9·6	13	19·8	—	14·80	3803	26
France	2·6	7·2	12·8	16·9	20	13·03	3445	300
Belgium	1·92	6·7	10·5	15·1	16	14·37	4032	67
Austria-Hungary	3·45	8·15	8·3	11·2	13	15·74	3909	222
Russia	2·7	8·25	6	9·1	12	16·37	2230	289
Spain	0·77	8·15	4·5	5·4	—	11·88	3439	32
Portugal	—	—	6	6·2	—	—	—	—
Greece	2·4	8·15	3	3·8	—	—	—	—
Roumania	—	—	3·5	4·1	—	14·53	2392	6
Turkey	5·47	9·6	3·5	5·7	—	—	—	—
Italy	6·7	14·4	2·8	3·9	5	11·27	3378	41
Servia	3·17	7·7	3	3·5	—	—	—	—

[1] The Fiscal System in Germany from 1841 to 1866 was based on the quantity of beets, the object being to bring about improvements in the cultivation of the beet and hence increase in the sugar-content; the tax corresponded with about 18*s*. per quintal, and was refunded to the manufacturer for all exported sugar. From 1870 to 1886 the tax was 1*s*. 7*d*. per quintal of beet, it being assumed that 12·5 kilos of beet were required to give 1 kilo of sugar, but even in 1870 1 kilo of sugar could be obtained from 11·9 kilos of beet, and in 1887 from 8·1 kilos. Since the exports increased enormously and the taxes refunded remained the same, the manufacturers enjoyed indirectly a considerable export bounty, which diminished the Exchequer receipts from £3,000,000 to less than £760,000 (1888). A modification was hence made in the system of taxation, sugar produced and consumed at home paying a tax of £1 per quintal, while that exported was freed from tax and received a bounty of 2*s*. 6*d*. (raw) or 3*s*. 6*d*. (refined) per 100 kilos (1896–1903). Further, the import duty was left at £2 per quintal, so that German producers were allowed to sell their sugar at high prices at home (even during the abundance of 1900–1901) and to employ part of their profits to lower the price of sugar sold abroad in competition with other countries. After the Brussels Convention, however, export bounties ceased and the import duty was reduced, to 5*s*. + 16*s*. (manufacturing tax in Germany). Under these new conditions,

DETERMINATION OF SUGAR-CONTENT. Sugar is estimated in various ways. With an aqueous sugar solution, the content of saccharose may be determined by means of the specific gravity at 17·5°, compared with water at 17·5°, this being measured by hydrometers, pyknometers, etc. (*see* Vol. I., p. 75). In the factory, use is generally made of a hydrometer (*saccharometer*) which, at 17·5°, gives directly the percentage of saccharose present.

These saccharometers were first proposed by Balling and were subsequently corrected by Brix, degrees Brix expressing the percentage of sugar. In France and Belgium, and sometimes also in Germany, saccharometers gauged at 15° and referred to water at 15° are used, and the Berlin Royal Commission for the control of standards prescribed the use of saccharometers giving the density of solutions at 20° referred to that of water at 4°.

The following Table gives the densities and degrees Brix (grms. of sugar per 100 grms. of solution) for the temperature 17·5°, and also, for each 10°, the values from the other two Tables, so that the intermediate values in these two Tables can be calculated roughly, The saccharometer is read with the precautions and in the manner indicated on p. 77 of Vol. I. and on p. 174 of this volume. The Table gives densities above 66° Brix, which cannot be determined by hydrometers, but which serve to calculate the degree of purity of impure saccharine solutions (molasses, etc. ; *see later*).

MATEGCZEK AND SCHEIBLER'S TABLE, GIVING THE SPECIFIC GRAVITIES AND DEGREES BRIX OF SACCHARINE SOLUTIONS.

Sp. gr. at $\frac{17·5°}{17·5°}$	Degrees Brix	Sp. gr. at $\frac{17·5°}{17·5°}$	Degrees Brix	Sp. gr. at $\frac{17·5°}{17·5°}$	Degrees Brix	Sp. gr. at $\frac{17·5°}{17·5°}$	Degrees Brix	Sp. gr. at $\frac{17·5°}{17·5°}$	Degrees Brix
1·00388	1	1·08778	21	1·18460	41	1·29531	61	1·42258	81
1·00779	2	1·09257	22	1·18981	42	1·30177	62	1·42934	82
1·01173	3	1·09686	23	1·19505	43	1·30777	63	1·43614	83
1·01570	4	1·10145	24	1·20033	44	1·31381	64	1·44298	84
1·01970	5	1·10607	25	1·20565	45	1·31989	65	1·44986	85
1·02373	6	1·11072	26	1·21100	46	1·32601	66	1·45678	86
1·02779	7	1·11541	27	1·21639	47	1·33217	67	1·46374	87
1·03187	8	1·12013	28	1·22182	48	1·33836	68	1·47074	88
1·03599	9	1·12488	29	1·22728	49	1·34460	69	1·47778	89
1·04014	10	1·12967	30	1·23278	50	1·35088	70	1·48406	90
1·01027 $\left[\frac{15°}{15°}\right]$	10	1·12999 $\left[\frac{15°}{15°}\right]$	30	1·23330 $\left[\frac{15°}{15°}\right]$	50	1·35182 $\left[\frac{15°}{15°}\right]$	70	1·48716 $\left[\frac{15°}{15°}\right]$	90
1·038143 $\left[\frac{20°}{4°}\right]$	10	1·126984 $\left[\frac{20°}{4°}\right]$	30	1·229567 $\left[\frac{20°}{4°}\right]$	50	1·347174 $\left[\frac{20°}{4°}\right]$	70	1·479976 $\left[\frac{20°}{4°}\right]$	90
1·04431	11	1·13449	31	1·23832	51	1·35720	71	1·49109	91
1·04852	12	1·13934	32	1·21300	52	1·36355	72	1·49915	92
1·05276	13	1·14423	33	1·24951	53	1·36995	73	1·50635	93
1·05703	14	1·14915	34	1·25517	54	1·37639	74	1·51359	94
1·06133	15	1·15411	35	1·26086	55	1·38287	75	1·52087	95
1·06566	16	1·15917	36	1·26658	56	1·38939	76	1·52810	96
1·07002	17	1·16413	37	1·27235	57	1·39595	77	1·53550	97
1·07441	18	1·16920	38	1·27816	58	1·40254	78	1·54290	98
1·07884	19	1·17430	39	1·28400	59	1·40918	79	1·55040	99
1·08329	20	1·17943	40	1·28989	60	1·41586	80	1·55785	100
1·08354 $\left[\frac{15°}{15°}\right]$	20	1·17985 $\left[\frac{15°}{15°}\right]$	40	1·29056 $\left[\frac{15°}{15°}\right]$	60	1·41628 $\left[\frac{15°}{15°}\right]$	80	1·56165 $\left[\frac{15°}{15°}\right]$	100
1·080959 $\left[\frac{20°}{4°}\right]$	20	1·176447 $\left[\frac{20°}{4°}\right]$	40	1·286456 $\left[\frac{20°}{4°}\right]$	60	1·411715 $\left[\frac{20°}{4°}\right]$	80	1·551800 $\left[\frac{20°}{4°}\right]$	100

If the degrees Brix are read with solutions at temperatures other than the normal, corrections must be made by means of the following Tables :

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the exports diminished somewhat, but the home consumption increased owing to the lowered prices. The wholesale price in 1910 was £2 per quintal (that of sugar for export, without tax, being 19*s*.) ; the retail price was 14*d*. per kilo in 1875, 7*d*. in 1902, and 6*d*. in 1910. The German Government received £5,750,000 in sugar taxes in 1900–1901, almost £8,000,000 in 1909–1910, and over £9,000,000 in 1913. In 1912 the manufacturing tax was 23*s*. 6*d*. per quintal. Diminution of the tax by 33 per cent. increased the consumption by 60 per cent.

STAMMER'S TABLE FOR REDUCING TO 17·5° DEGREES BRIX READ AT DIFFERENT TEMPERATURES.

Temperature		Degrees Brix of the Solutions											
		5	10	15	20	25	30	35	40	50	60	70	75
13°	These corrections to be subtracted from the observed Brix degrees	0·18	0·19	0·21	0·22	0·24	0·26	0·27	0·28	0·29	0·33	0·35	0·39
15°		0·11	0·12	0·14	0·14	0·15	0·16	0·17	0·17	0·17	0·19	0·21	0·25
17°		0·02	0·03	0·03	0·03	0·04	0·04	0·04	0·04	0·04	0·05	0·05	0·06
18°	These corrections to be added to the observed Brix degrees	0·03	0·03	0·03	0·03	0·03	0·03	0·03	0·03	0·03	0·03	0·03	0·02
19°		0·08	0·08	0·09	0·09	0·10	0·10	0·10	0·10	0·10	0·10	0·08	0·06
21°		0·20	0·22	0·24	0·24	0·25	0·25	0·25	0·26	0·26	0·25	0·22	0·18
23°		0·32	0·35	0·37	0·38	0·39	0·39	0·39	0·40	0·42	0·39	0·36	0·33
25°		0·44	0·47	0·49	0·51	0·53	0·54	0·55	0·55	0·58	0·54	0·51	0·48

Example.—If a sugar solution shows 40° Brix (*i.e.*, 40 per cent. of sugar) at a temperature of 23°, 0·4 must be added to reduce the reading to the true Brix degrees at 17°; so that 40 + 0·4 = 40·4 degrees Brix at 17°.

SCHEIBLER'S TABLE SHOWING DEGREES BRIX AT 15° AND THE CORRESPONDING DEGREES AT OTHER TEMPERATURES (FROM 10° TO 25°).

Temperature	Degrees Brix or Percentage of Sugar											
10° .	5·15	10·19	15·22	20·24	25·27	30·29	35·30	40·31	50·33	60·35	70·36	75·36
12° .	5·10	10·12	15·14	20·15	25·17	30·18	35·18	40·19	50·20	60·21	70·21	75·21
14° .	5·04	10·04	15·05	20·05	25·06	30·06	35·06	40·07	50·07	60·07	70·07	75·07
15° .	5·00	10·00	15·00	20·00	25·00	30·00	35·00	40·00	50·00	60·00	70·00	75·00
17° .	4·92	9·91	14·90	19·89	24·88	29·87	34·87	39·87	49·86	59·86	69·86	74·86
19° .	4·83	9·80	14·78	19·77	24·75	29·74	34·73	39·73	49·72	59·71	69·71	74·71
21° .	4·72	9·69	14·66	19·64	24·62	29·60	34·59	49·50	49·57	59·57	69·57	74·57
23° .	4·61	9·57	14·53	19·50	24·48	29·46	34·45	39·44	49·42	59·42	69·42	74·42
25° .	4·49	9·44	14·40	19·36	24·34	29·32	34·30	39·29	49·27	59·27	69·27	74·28

Example.—If a solution reads 19·36° Brix at a temperature of 25°, this would correspond with 20° Brix at the normal temperature of 15°. For intermediate values, either of temperature or of concentration, the corresponding results are easily obtained by interpolation. Thus, 18° Brix at temperature 15° would give, at other temperatures, values higher than those corresponding with 15° Brix by three-fifths of the difference between the values in the 15° Brix and 20° Brix columns. So that a solution showing 18° Brix at the temperature 15° would show, at the temperature 17°, $14{\cdot}90 + \frac{3}{5}(19{\cdot}89 - 14{\cdot}90) = 14{\cdot}90 + 2{\cdot}99 = 17{\cdot}89°$ Brix.

In the quantitative determination of sugar, use is commonly made of its action on polarised light (*see* p. 28), this being measured in the *polarimeter*. The rotatory power of a sugar solution is proportional to the concentration and almost independent of the temperature. In these determinations it is necessary to use pure sugar solutions, decolorised by means of a little basic lead acetate (or, better, mercuric acetate or phosphotungstic acid), which precipitates the albuminoids, colouring-matters, and other impurities; the filtered solution is examined in the polarimeter. If the saccharose is accompanied by another optically active sugar—for instance, glucose (dextro-rotatory)—allowance must be made for the rotation of the latter. In such a case the diminution in rotation produced by inversion of the saccharose with dilute acid would give the amount of this sugar.

The use of the refractometer for the estimation of sugar has also been proposed (*see* p. 463; also Villavecchia, "Applied Analytical Chemistry," Vol. II., p. 93).

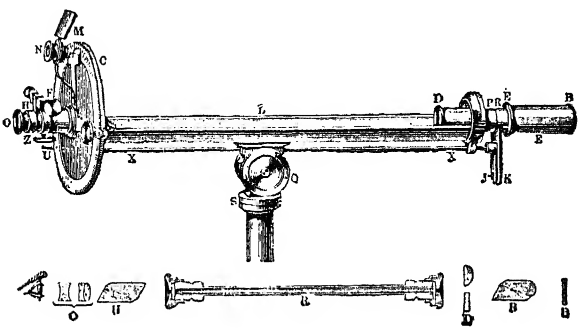


FIG. 374.

POLARIMETERS AND SACCHARIMETERS.[1] One of the best-known polarimeters is the Laurent shadow instrument (Fig. 374), which contains, in place of the compensator and double-polarisation quartz plate, a special semicircular quartz plate, *D*, half a wave-length in thickness and occupying one-half of the field. The polariser, *B*, is rotated by means of the rod, *X*, and the rotation which restores the two halves of the field to the same luminosity is indicated on a graduated circle, *C*, provided with a vernier, read by means of the lens, *N*, and illuminated by the mirror, *M*.

[1] It has been mentioned already (*see* p. 27) that crystals of Iceland spar and quartz have the property of decomposing a ray of light into two polarised rays, the ordinary and the extra-ordinary. If a prism of Iceland spar with length greater than the breadth, with its acute angle of 68°, is cut diagonally and lengthwise so as to divide it into two rectangular triangular prisms (Fig. 375), and these are cemented together again with Canada balsam, the result is a Nicol prism. When a ray of light, *lm*, enters the *nicol*, of the two refracted rays (*mo*, *mp*), the ordinary one, *mo*, is totally reflected by the layer of Canada balsam and is thrown out of the crystal (*or*), whilst the extraordinary ray, *mp*, passes through the prism (*pqs*) and emerges polarised. This ray is able subsequently to traverse a second nicol only when the principal section of this *analysing nicol* is parallel to that of the first *polarising nicol*. If, on the other hand, the two principal sections are perpendicular, the ray undergoes total reflection and will not pass through the second nicol; in intermediate positions, varying quantities of light are allowed to pass. If a layer of water is placed between the perpendicular nicols, still no light will pass through the analyser, but if a sugar solution is interposed, the light passes with a greater or less intensity through the analyser, which must be rotated through a certain angle (proportional to the quantity of sugar) to produce total disappearance of the light. In order to determine exactly

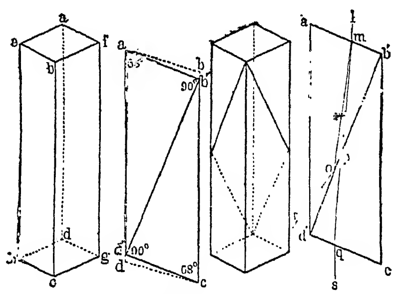


FIG. 375.

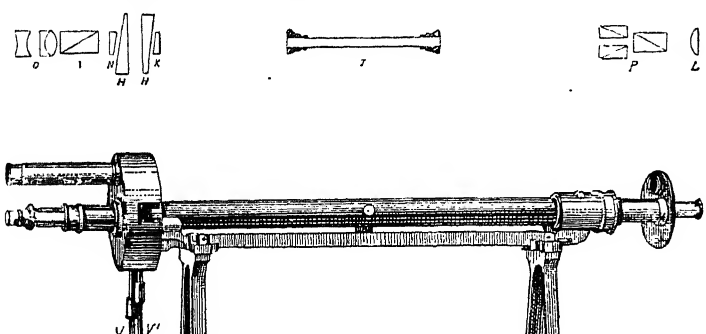


FIG. 376.

when the luminous ray is extinguished (even in this case a kind of half-shadow is always observed), Soleil attempted to divide the luminous field into two halves with complementary colours. Indeed, if a ray of polarised light is passed through a quartz plate placed between the two nicols, one half of this plate being dextro- and the other lævo-rotatory, and the junction of the two lying exactly on the axis of the light, the two halves of the field will appear illuminated with complementary colours. If the plate is 3·75 mm. in thickness and the analyser is rotated through

The source of monochromatic light is a double bunsen flame coloured with sodi chloride, the light being collected by the lens, *B*, and the observation made through eye-piece, *O*. The scale of the apparatus is regulated by the screw, *Z*, so that it reads z when the two halves of the field are equally illuminated. If a tube containing a liqu interposed between the two nicols, causes the right-hand half of the field to darken, liquid is dextro-rotatory, while darkening of the left-hand half indicates a lævo-rotat compound. From the rotation read on the scale, the specific rotation may be calcula by the formulæ given on p. 28.

The practical examination of sugars is made with polarimeters furnished with spec scales and known as *saccharimeters;* the Laurent polarimeter has a saccharimetric grad tion as well as that showing circular degrees.

In the French saccharimeters (Soleil and Laurent) the 100 division corresponds w a normal aqueous solution of pure saccharose (obtained by precipitation of a very conc trated aqueous solution with alcohol and drying at 60° to 70°) containing 16·350 grms. 100 c.c. at 17·5°, the reading being made in a tube 20 cm. long (the same reading is giv by a quartz plate 1 mm. in thickness). In the German instruments (Ventzke-Scheibl Schmidt and Haensch) the 100 reading is obtained with a length of 20 cm. of a sacchar solution of sp. gr. 1·1, which contains 26·048 grms. per 100 c.c. at the temperature 17·5 Thus, a reading of one division corresponds with 0·26048 grm. of saccharose per 100 c.c., 1 grm. of sugar per 100 c.c. gives a reading of 3·839 divisions.

The source of light for modern saccharimeters is an incandescent gas-burner enclos in a blackened metal chimney fitted with a ground-glass window, or an incandesce electric lamp of at least 32 candle-power with a ground-glass globe and also enclosed in black case. In order that the apparatus may n become heated, the lamp should be placed at distance of about 15 cm., and to render the lumino fields more distinct the light is passed first throu a glass cell with parallel walls filled with 6 per ce bichromate solution in a layer 15 mm. thick; this way the more refractive rays are absorbed a a uniform yellow light obtained. The norm tube of the saccharimeter contains a column liquid exactly 20 cm. long, but for very dilute and slightly rotating solutions tubes of 30, 4 and 50 cm. are used, whilst for solutions which are not quite colourless tubes of 10 or 5 c may be employed; in all cases the readings are referred to the normal length of 20 c Some tubes are provided with an aperature for the introduction of a thermometer, so th the temperature of the solution may be read in the instrument.

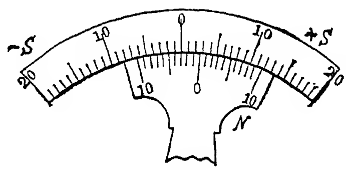


FIG. 377.

The saccharimeter scale extends from 0 to 100 divisions on the positive side and t — 30 on the negative side. The integral divisions are given by the zero of the vernier, (Fig. 377), and the decimal parts by that division of the vernier scale which coincides exactl with a division on the scale; in Fig. 377 the reading is + 2·6 divisions.[2]

24·5°, the two halves of the field are almost completely extinguished and assume a pale r coloration, similar in the two halves. If, however, a sugar solution is interposed, the two halv assume different colours, extinction being restored by rotation of the analysing nicol. Lat Soleil suggested compensating the rotation of the sugar solution by introducing, to a great or less extent, between the nicols, a conical quartz plate or *compensator*, moved by a rack indicatin on a scale the thickness of the plate and hence the equivalent rotation. The more mode saccharimeters of the Soleil-Ventzke type have two compensators, each formed of two quart wedges (*MN* and *HK*, Fig. 376) of opposite rotations, and are fitted also with the Lippich *polaris* formed of three nicols (*P*), which give a field divided into three zones; when these zones a not equally illuminated, the two lateral ones show a colour different from that of the middle on The analyser is enclosed in a metal box to protect it from dust. The two compensators wit their scales are regulated by two screws, *V* and *V′*. When the two scales indicate zero, the thr zones should be equally illuminated.

[1] That is, in 100 Mohr c.c., 1 Mohr c.c. being the volume of 1 grm. of water at 17·5° weighe in air with brass weights. The *true* c.c. is the volume of 1 grm. of water at 4° weighed *in vacuo* calculation on the basis of the coefficient of expansion of water shows that 100 Mohr c.c. ar equal to 100·234 true c.c., so that 100 *true* c.c. of the normal saccharose solution at 17·5° woul contain 25·987 grms. of saccharose. The International Commission for uniform methods of suga analysis proposed in 1900 the fixing of the 100 point of the saccharimeter by a length of 20 cm of a solution obtained by dissolving 26 grms. of pure saccharose in water to a volume of 10 *true* c.c. at 20° and polarising at 20° (100 true c.c. of water at 20° weigh 99·7174 grms. in ai and 99·8294 grms. *in vacuo*).

[2] With double compensation saccharimeters (furnished with two scales, a *working* scal

The specific rotatory power of saccharose varies little with the concentration (up to 30 per cent.) and with the temperature (between 15° and 25°), but it is best to work near to 20°, when $[\alpha]_D^{20} = +66{\cdot}5°$.[1]

and a *control*, *V* and *V′*, Fig. 376) the procedure is as follows: When the tube with the sugar solution is introduced between the nicols the control scale is placed at zero, the working scale being then moved by the screw until the field is uniformly illuminated and its position read. The sugar solution is next removed and the control scale moved until the field is again uniform, the reading of this scale being nearly equal to the first reading of the working scale. The tube of solution is now again introduced and the position of the working scale, near to the zero-point, read after its adjustment to give uniform luminosity. Finally the tube is again removed and the control scale moved until the field is uniform and its position read. The final result is obtained by subtracting the mean of the second pair of readings from the mean of the first pair. Thus, if the readings were + 78·6, + 78·4, + 0·2, and − 0·3, the result would be 78·5 + 0·05 = + 78·45.

[1] CONSTANTS OF THE PRINCIPAL SUGARS.

Sugar	$[\alpha]_D^{20}$	Number of grms. per 100 c.c. giving rotation of one division.			Number of divisions for 1 grm. in 100 c.c.			Number of grms. which reduce 100 c.c. of Fehling's solution.		Number of c.c. of Fehling's solution reduced by 1 grm.	
		Circular degrees (true c.c.)	Ventzke divisions (true c.c.)	Ventzke divisions (Mohr c.c.)	Circular degrees (true c.c.)	Ventzke divisions (true c.c.)	Ventzke divisions (Mohr c.c.)	Non-diluted	Diluted with 4 vols. of water.	Non-diluted	Diluted with 4 vols. of water.
Saccharose .	+66·5	0·7519	0·2600	0·26048	1·330	3·846	3·839	—	—	—	—
Invert sugar	−20·2	2·475	0·8380	0·8395	−0·404	−1·193	−1·191	0·494	0·515	202·4	194
Glucose .	+52·8	0·947	0·3275	0·3281	1·056	3·053	3·048	0·475	0·4945	210·4	202·2
Levulose .	−93·0	0·5376	0·1838	0·1841	−1·860	−5·439	−5·430	0·514	0·537	194·4	186
Maltose .	+138·2	0·3618	0·1255	0·1258	2·764	7·968	7·949	0·779	0·741	128·4	135
Lactose (hydrated)	+52·53	0·9518	0·3288	0·3295	1·051	3·041	3·035	0·676	0·676	148	148
Raffinose (hydrated)	+104·5	0·4785	0·16545	0·16576	2·090	6·044	6·033	—	—	—	—
(anhydrous)	+123·1	0·406	0·14039	0·14065	2·463	7·123	7·110	—	—	—	—

Invert sugar has a rotatory power varying markedly with the concentration and temperature. A solution of saccharose containing the normal weight (26·048 grms.) contains, after inversion, 27·419 grms. of invert sugar, and if this is contained in 100 c.c. it gives a deviation of − 32·66 in a 20 cm. tube at 20°. The variation per degree of temperature is 0·5, so that at 0° this reading would be − 42·66 and, in general, at any temperature, *t*, it would be $-42{\cdot}66 + 0{\cdot}5\,t$. If no account is taken of variations due to the concentration, 1 division Ventzke corresponds with 0·8395 grm. of invert sugar in 100 c.c. (Mohr), the solution being read in a 20 cm. tube at 20°; or 1 grm. of invert sugar dissolved in 100 Mohr c.c. gives a reading of − 1·191 division. The specific rotatory power of invert sugar for different concentrations (from 1 to 35 per cent.) is given by the formula: $[\alpha]_D^{20} = -19{\cdot}657 - 0{\cdot}03611c$, *c* indicating the weight of invert sugar in 100 c.c. For concentrations near 15 per cent. the value − 20·2° may be taken for the specific rotation of invert sugar, 1 *circular* degree then corresponding with 2·475 grm. of invert sugar in 100 true c.c. and 1 grm. of invert sugar in 100 true c.c. giving a rotation in circular degrees of − 0·404.

Glucose has the specific rotation, $[\alpha]_D^{20} = +52{\cdot}8°$, which is constant after *muta-rotation* has ceased (*see* p. 28), *i.e.*, if the observation is made after the solution has been either left for 24 hours or boiled for 15 minutes. The concentration and the temperature have virtually no influence on the rotatory power.

For *fructose* (*levulose*) the data are uncertain owing to the difficulty of obtaining pure crystals, and the rotatory power varies with the concentration (for solutions of about 10 per cent. strength, $[\alpha]_D^{20} = -93°$) and with the temperature (an increase of 1° of temperature diminishes the specific rotatory power by 0·67°).

Lactose. For $C_{12}H_{22}O_{11} + H_2O$, after the disappearance of the muta-rotation, the specific rotation, which is but slightly influenced by the concentration, is $[\alpha]_D^{20} = +52{\cdot}53°$; this diminishes by 0·075° for every degree rise in temperature.

Maltose has a specific rotation (after muta-rotation has been destroyed; *see* Glucose) varying with the temperature and concentration according to the equation: $[\alpha]_D^t = 140{\cdot}375 - 0{\cdot}01837\,c - 0{\cdot}095\,t$, where *t* indicates the temperature and *c* the percentage by weight of anhydrous maltose. For medium concentrations, $[\alpha]_D^{20} = +138{\cdot}2°$.

Raffinose, $C_{18}H_{32}O_{16} + 5H_2O$, has the specific rotation, $[\alpha]_D^{20} = +104{\cdot}5°$, which is almost independent of the temperature and concentration.

CHEMICAL DETERMINATION OF SUGARS. With the exception of saccharose and raffinose, the sugars (glucose, levulose, etc.) reduce Fehling's solution (an alkaline solution of copper sulphate containing salts of organic hydroxy-acids ; *see* pp. 255 and 400) in the hot, with separation of a corresponding amount of cuprous oxide.[1]

NON-SUGAR, APPARENT DENSITY, TRUE DENSITY, AND QUOTIENT OF PURITY. Sugars and their solutions are distinguished, commercially and industrially, by their content of saccharose, water, and *solids not sugar* (*e.g.*, salts and various organic substances).

The Brix saccharometer is graduated with pure sugar solutions, and hence gives results which are increasingly inaccurate as the degree of impurity of the sugar solutions increases.

[1] Fehling's solution is obtained by mixing, just before using, equal volumes of the two following solutions : (*a*) 69·278 grms. of pure crystallised copper sulphate ($CuSO_4 + 5H_2O$), air-dried until constant in weight, dissolved in water to 1 litre ; (*b*) 346 grms. of Rochelle salt (sodium potassium tartrate) and 100 grms. of pure solid sodium hydroxide dissolved in water to 1 litre. Since saccharose does not reduce Fehling's solution, it must be first inverted. For this purpose, 9·5 grms. of the sugar are dissolved in 700 c.c. of N/3-hydrochloric acid and the solution heated for 30 minutes in a water-bath at 75°, neutralised with caustic soda, and made up to 1 litre. This solution, which contains 10 grms. of invert sugar, is then ready for testing.

The Fehling test may be either volumetric or gravimetric, the concentration of the sugar being reduced to about 1 per cent. (by a preliminary trial) and the details of the procedure being followed exactly. *Volumetric method* : 40 c.c. of water and 10 c.c. of Fehling's solution (5 c.c. of each of the component solutions) are brought to boiling in an Erlenmeyer flask, a measured quantity (4 to 5 c.c.) of the sugar solution run in from a burette, and the liquid again heated and kept boiling for a definite time (two minutes for glucose or invert sugar, four minutes for maltose, and six for lactose) ; the flame is then removed, a few drops of the liquid filtered, and the filtrate acidified with a little acetic acid and tested with a drop of potassium ferrocyanide solution. If a red coloration is produced, the test is repeated with a larger quantity of sugar solution, whilst if no red coloration appears, a less quantity of the sugar is tried. This procedure is continued until in the last two tests, representing excess and deficiency of the sugar solution, the difference between the two volumes is not more than 0·1 c.c. ; the mean of these two volumes is employed in calculating the sugar-content of the solution. 100 c.c. of undiluted Fehling's solution, under the above conditions, corresponds with 0·4945 grm. of glucose, 0·533 of levulose, 0·515 of invert sugar, 0·740 of maltose, and 0·676 of lactose (hydrated).

The *gravimetric estimation* is carried out as follows (Allihn's method) : To 60 c.c. of Fehling's solution, diluted with 60 c.c. of boiled distilled water and heated to boiling, are added 25 c.c. of the sugar solution of about 1 per cent. concentration, the liquid being then again heated and kept boiling for a definite time (two minutes for glucose, levulose, and invert sugar, four for maltose, and six for lactose). The solution is then filtered at once, with the aid of a filter-pump, through a dried and weighed Soxhlet tube containing a layer of asbestos, the cuprous oxide being repeatedly washed with a total quantity of 300 to 400 c.c. of boiling water, then with two or three portions of alcohol, and finally with ether. The tube is then dried in an oven, and the cuprous oxide subsequently reduced to metallic copper by passing a current of dry hydrogen through the tube and gently heating the oxide with a small flame ; the hydrogen is kept passing until the tube is quite cold, when the weight is taken. From the weight of copper thus obtained, the corresponding weight of sugar is read off from the following Table, all the numbers representing milligrams :

Copper	Glucose	Invert sugar	Maltose	Lactose	Copper	Glucose	Invert sugar	Maltose	Lactose	Copper	Glucose	Invert sugar	Maltose	Lactose
30	16	—	25·3	—	155	79·1	81·6	135·9	112·6	280	145·5	151·9	247·8	208·3
35	18·5	—	29·6	—	160	81·7	84·3	140·4	116·4	285	148·3	154·9	252·2	212·3
40	20·9	—	33·9	—	165	84·3	87·0	144·9	120·2	290	151·0	157·8	256·5	216·3
45	23·4	—	38·3	—	170	86·9	89·7	149·4	123·9	295	153·8	160·8	261·1	220·3
50	25·9	—	42·6	—	175	89·5	92·4	153·8	127·8	300	156·5	163·8	265·5	224·4
55	28·4	—	47·0	—	180	92·1	95·2	158·3	131·6	305	159·3	166·8	269·9	228·3
60	30·8	—	51·3	—	185	94·7	97·8	162·7	135·4	310	162·0	169·7	—	232·2
65	33·3	—	55·7	—	190	97·3	100·6	167·2	139·3	315	164·8	172·7	—	236·1
70	35·8	—	60·1	—	195	100·0	103·4	171·6	143·1	320	167·5	175·6	—	240·0
75	38·3	—	64·5	—	200	102·6	106·3	176·1	146·9	325	170·3	178·6		243·9
80	40·8	—	68·9	—	205	105·3	109·1	180·5	150·7	330	173·1	181·6	—	247·7
85	43·4	—	73·2	—	210	107·9	111·9	185·0	154·5	335	175·9	184·7	—	251·6
90	45·9	46·9	77·7	—	215	110·6	114·7	189·5	158·2	340	178·7	187·8	—	255·7
95	48·4	49·5	82·1	—	220	113·2	117·5	193·9	161·9	345	181·5	190·8	—	259·8
100	50·9	52·1	86·6	71·6	225	115·9	120·4	198·4	165·7	350	184·3	193·8	—	263·9
105	53·5	54·8	91·0	75·3	230	118·5	123·2	202·9	169·4	355	187·2	196·8	—	268·0
110	56·0	57·5	95·5	79·0	235	121·2	126·0	207·4	173·1	360	190·0	199·8	—	272·1
115	58·6	60·1	99·9	82·7	240	123·9	128·9	211·8	176·9	365	192·9	203·0	—	276·2
120	61·1	62·8	104·4	86·4	245	126·6	131·8	216·3	180·8	370	195·7	206·1	—	280·5
125	63·7	65·5	108·9	90·1	250	129·2	134·6	220·8	184·8	375	198·6	209·2	—	284·8
130	66·2	68·1	113·4	93·8	255	131·9	137·5	225·3	188·7	380	201·4	212·4	—	289·1
135	68·8	70·8	117·9	96·6	260	134·6	140·4	229·8	192·5	385	204·3	215·5	—	293·4
140	71·3	73·5	122·4	101·3	265	137·3	143·2	234·3	196·4	390	207·1	218·7	—	297·7
145	73·9	76·1	126·9	105·1	270	140·0	146·1	238·8	200·3	395	210·0	221·8	—	302·0
150	76·5	78·9	131·4	108·8	275	142·8	149·0	243·3	204·3	400	212·9	224·9	—	306·3

Apparent density is that shown by the Brix hydrometer, while the *real density* corresponds with the true content of sugar determined by direct analysis (by the polarimeter or, after inversion, by Fehling's solution). The difference between the real and apparent densities, expressed in degrees Brix, indicates the *non-sugar* in Brix degrees, while the *ratio* between the real and apparent densities, in degrees Brix, is termed the *quotient of purity* and, when multiplied by 100, shows the percentage of sugar present independently of the water.

In the *analysis of a mixture of various sugars* a number of optical and chemical tests must be made in order to deduce, directly or indirectly, the quantities of the separate components (*see* Villavecchia, " Applied Analytical Chemistry," Vol. II., pp. 114 *et seq.*[1]).

[1] If only saccharose and another sugar are present, p grms. of the mixture are dissolved in water to 100 c.c. and the polarisation, P, read; if a_1 is the rotation of 1 grm. of saccharose per 100 c.c. and a_2 that of 1 grm. of the other sugar, the quantities x and y of saccharose and the other sugar respectively are given by the formulæ: (I) $x = \frac{P - a_2 p}{a_1 - a_2}$, (II) $y = \frac{a_1 p - P}{a_1 - a_2}$, since $x + y = p$ (III) and $a_1 x + a_2 y = P$ (IV). The values of a_1, a_2, and P must be given their proper algebraic signs (+ or —).

(*A*). In the special case of a *mixture of saccharose and glucose*, the components x and y may be determined in various ways:

(1) The glucose (y) may be estimated by means of Fehling's solution; formula IV then gives $x = \frac{P - a_2 y}{a_1}$ (V). Since saccharose reduces Fehling's solution to a very slight extent, small proportions of glucose are best determined by means of Soldaini's reagent, which consists of 150 grms. of potassium bicarbonate, 104·4 grms. of normal potassium carbonate, and 100 c.c. of the copper sulphate solution used for Fehling's solution, made up to a litre with water.

(2) The solution of the mixture is polarised (P), the saccharose being inverted and the polarisation again read (P_1). If a_3 is the rotation of 1 grm. of invert sugar (= — 1·191), then, since 1 grm. of saccharose gives 1·053 grm. of invert sugar, we have $1{\cdot}053\, a_3 x + a_2 y = P_1$ (VI) and hence $x = \frac{P - P_1}{a_1 - 1{\cdot}053 a_3}$ (VII) and $y = \frac{a_1 P_1 - 1{\cdot}053 a_3 P}{a_2(a_1 - 1{\cdot}053 a_3)}$ (VIII), a_1 having the value 3·839 and a_2 3·057, it follows that $x = \frac{P - P_1}{5{\cdot}093}$ (IX) and $y = \frac{3{\cdot}839 P_1 + 1{\cdot}254 P}{5{\cdot}093 \times 3{\cdot}057}$ (X), which are the quantities of the two sugars in p grms. of the mixture. The percentages will therefore be $\frac{100x}{p}$ and $\frac{100y}{p}$ respectively. For a mixture of *saccharose* and *levulose*, $a_2 = -5{\cdot}439$, so that $y = \frac{-3{\cdot}839 P_1 - 1{\cdot}254 P}{27{\cdot}701}$; for *saccharose* and *invert sugar*, $a_2 = -1{\cdot}191$ and the denominator becomes 6·066 instead of 27·701; for *mixtures of saccharose and maltose*, $a_2 = 7{\cdot}949$ and $y = \frac{3{\cdot}839 P_1 + 1{\cdot}254 P}{5{\cdot}093 \times 7{\cdot}949}$; for *saccharose* and *lactose hydrate*, $a_2 = 3{\cdot}035$.

(3) The glucose is first determined by means of Fehling's solution; in another portion of the solution the saccharose is inverted and the reducing sugars again estimated with Fehling's solution: the difference between these two estimations gives the invert sugar and this, multiplied by 0·95, the saccharose.

(*B*). With a *mixture of saccharose and raffinose*, the polarisation is determined before (P) and after (P_1) inversion; a_1 and a_2 being the known rotations of 1 grm. of each of the two sugars and a_3 and a_4 those of 1 grm. of the respective inverted products, it follows that: $a_1 x + a_2 y = P_1$ (XIII) and $1{\cdot}053\, a_3 x + 1{\cdot}036\, a_4 y = P_1$ (XIV); substitution in these of the values $a_1 = 3{\cdot}839$, $a_2 = 7{\cdot}11$, $1{\cdot}053\, a_3 = -1{\cdot}254$ and $1{\cdot}036\, a_4 = 3{\cdot}643$ gives $x = \frac{0{\cdot}5124 P - P_1}{3{\cdot}2211}$ and $y = \frac{1{\cdot}254 P + 3{\cdot}839 P_1}{22{\cdot}9}$. For the determination of the raffinose by means of methyl-phenylhydrazine, in presence of saccharose and invert sugar, *see* Raffinose, p. 585.

(*C*). When two reducing sugars but neither saccharose nor raffinose is present, it is sufficient to measure the polarisation and apply formulæ I to IV. But if a non-saccharine substance is also present, it is necessary to determine also the number (F) of c.c. of Fehling's solution reduced by a weight, p, of the substance; if b_1 and b_2 are the volumes (c.c.) of Fehling's solution reduced by 1 grm. of each of the two sugars dissolved in 100 c.c., then: $a_1 x + a_2 y = P$ (XV) and $b_1 x + b_2 y = F$ (XVI) and hence $x = \frac{b_2 P - a_2 F}{a_1 b_2 - a_2 b_1}$ and $y = \frac{a_1 F - b_1 P}{a_1 b_2 - a_2 b_1}$. With a *mixture of glucose and levulose*, $a_1 = 3{\cdot}057$, $a_2 = -5{\cdot}439$, $b_1 = 202{\cdot}4$, and $b_2 = 186$, so that $x = \frac{186P + 5{\cdot}439F}{1669}$ and $y = \frac{3{\cdot}057F - 202{\cdot}4P}{1669}$. For *mixtures of glucose and maltose*, a_2 has the value 7·940 and b_2 135; these last two numbers hold also for mixtures of *invert sugar and maltose*, but then $a_1 = -1{\cdot}191$ and $b_1 = 194$; for *mixtures of glucose and lactose*, $a_1 = 3{\cdot}057$, $a_2 = 3{\cdot}035$, $b_1 = 202{\cdot}4$, and $b_2 = 148$, while for *invert sugar* and *lactose*, a_2 and b_2 have the values just given, but $a_1 = -1{\cdot}191$ and $b_1 = 194$.

(*D*). With a *mixture of saccharose* (x), *glucose* (y), *and levulose* (z), if a weight, p, is dissolved to 100 c.c., and a_1, a_2, a_3, a_4 represent the respective rotations of 1 grm. of each of these sugars and of invert sugar in 100 c.c., b_2 and b_3 the number of c.c. of Fehling's solution reduced by 1 grm. of each of the reducing sugars, P and P_1, the polarisations before and after

The total *ash* of a sugar is determined by weighing 3 grms. into a tared platinum dish, moistening it with a few drops of concentrated sulphuric acid, carbonising over a bunsen flame and incinerating in a muffle at a low red heat (about 700°) so that the ash does not fuse. From the sulphated ash, one-tenth of its weight is deducted in order to correct for the increase due to the formation of sulphates. By means of tables the quantity of *soluble ash* can also be deduced.

The water is determined by heating 5 to 10 grms. of the sugar in a flat glass dish covered with a clock-glass at 105° to 110° first for 2 hours and subsequently to constant weight. Subtraction from 100 of the water and the sugar gives the percentage of *total non-sugar*, while further subtraction of the ash gives the *organic non-sugar*. The *alkalinity* of the sugar is determined by titrating an aqueous solution of 20 grms. of the product with decinormal sulphuric acid in presence of phenolphthalein; the result is calculated as grams of CaO per 100 grms. of sugar.

PURIFICATION OF WASTE-WATERS FROM SUGAR-WORKS. The waters requiring purification, since they are highly contaminated and readily ferment, are those used in emptying and washing the diffusors, those from the pulp-presses and, partly, those in which the beets have been washed. The first contain up to 0·5 per cent. of suspended matter and 0·6 to 0·8 per cent. of dissolved organic matter, with about 0·3 per cent. of sugar; they have a bad smell, and it is usually prohibited to introduce them as they stand into streams.

Chemical purification (with lime or iron oxide or sulphate) is costly and insufficient, while the mechanical method of filtration to remove the suspended matter does something but only partially solves the problem. Biological purification (*see* Vol. I., p. 249), preceded by filtration or by aeration (omitting the septic tank) gives better results than the older processes, but is not entirely satisfactory (it eliminates 40 to 70 per cent. of the organic matter). The principal bacteria which destroy saccharose are *Leuconostoc* and *Clostridium*. The problem of the complete purification of these waste-waters still remains unsolved.

C. TRIOSES

RAFFINOSE, $C_{18}H_{32}O_{16} + 5H_2O$, forms pointed crystals and has a very high rotatory power ($[\alpha]_D^{20} = +104{\cdot}5°$), and since also saccharose containing

inversion, and F the number of c.c. of Fehling's solution reduced by weight p of the substance, then (XVII) $P = a_1x + a_2y + a_3z$; $P_1 = 1{\cdot}053\ a_4x + a_2y + a_3z$; $F = b_2y + b_3z$. The first two of these give $x = \frac{P - P_1}{a_1 - 1{\cdot}053a_4}$, which corresponds with formula VII. Then (XVIII) $a_2y + a_3z = P - a_1x$ and $b_2y + b_3z = F$, which are analogous to formula XV, allow of the determination of the values of y and z. Thus $x = \frac{P - P_1}{5{\cdot}093}$, and for y and z we have, in analogy to formula XVI (diminishing the polarisation, P, by the rotation of the saccharose, $3{\cdot}839x$), $y = \frac{233P + 714P_1 + 27{\cdot}7F}{8500}$ and $z = \frac{15{\cdot}57F - 254P - 777P_1}{8500}$. With a *mixture of saccharose* (x), *invert sugar* (y) *and lactose* (z), the saccharose is arrived at as above, and then:

$$y = \frac{15{\cdot}46F - 185{\cdot}6P - 568P_1}{3896} \text{ and } z = \frac{6{\cdot}066F + 243P + 745P_1}{3896}.$$

Practical Examples. 26·048 grms. of the sugar or mixed sugars are dissolved in a 100 c.c. flask and, if the solution is coloured, basic lead acetate solution (10 to 30 drops) is added drop by drop until it forms no further turbidity; the solution is made up to 100 c.c. with water, filtered through a dry filter and polarised in a 20 cm. tube, a drop of acetic acid being previously added, if necessary, to make the liquid clearer.

If it is thought desirable to eliminate the excess of lead acetate, the liquid is made up to volume with saturated sodium sulphate solution instead of with water.

In the case of a mixture of invert sugar and saccharose, if the normal weight solution gives a rotation of $+24{\cdot}0$ before and $-27{\cdot}0$ after inversion, the quantity of saccharose in 100 c.c. of the solution will be $\frac{24 + 27}{5{\cdot}093} = 10{\cdot}01$, and that of invert sugar $\frac{3{\cdot}839 \times 27 - 1{\cdot}254 \times 24}{6{\cdot}066} =$ 12·12 grms.

If other sugars are also present, the invert sugar is first determined with Fehling's solution, such quantity of the sugar solution being taken (after a preliminary trial) as contains about 0·2 grm. of invert sugar and the determination being made with 50 c.c. of Fehling's solution by the gravimetric method. The result is subject to a *slight* correction, according to a Table by Meissl and Hiller, for the influence of the saccharose on the Fehling's solution, but this only in cases where the invert sugar is present in relatively small proportion compared with the saccharose, as, for instance, when samples of saccharose are being analysed.

raffinose exhibits pointed crystals and an increased rotation, raffinose is known in Germany as *Spitzenzucker* or *Pluszucker*. It is a hexatriose, and when hydrolysed takes up $2H_2O$, giving equal proportions of *d*-glucose, *d*-fructose, and *d*-galactose. By restricting the hydrolysis, most suitably by effecting it with enzymes, an intermediate stage may be realised, consisting of *d*-fructose and *melibiose* (isomeric with lactose), which is subsequently resolved into *d*-glucose and *d*-galactose. Raffinose is found together with cane-sugar in the sugar-beet, its amount varying with the season. In the manufacture of saccharose, it accumulates in the molasses and often occurs abundantly in the sugar extracted from beet-molasses by the strontia process; in the final syrup from this treatment it occurs sometimes to the extent of 20 per cent. Raffinose does not give the reactions of the monoses (reduction of Fehling's solution, etc.), and hence contains no carbonyl group, its rational formula being

$$\underset{\text{Galactose}}{(C_6H_{11}O_5 \cdot O)} \cdot (\underset{\text{Glucose}}{C_6H_{10}O_4} \cdot O \cdot \underset{\text{Fructose}}{C_6H_{11}O_5}).$$

Melibiose, which, like lactose, exhibits the reactions of the monoses and contains a carbonyl group, is represented thus: $\underset{\text{Galactose}}{(C_6H_{11}O_5 \cdot O)} \cdot \underset{\text{Glucose}}{C_6H_{11}O_5}$. So that raffinose usually decomposes first at the point where a carbonyl group occurs (between glucose and fructose); otherwise it would yield a biose without a free carbonyl group. Indeed, Neuberg (1907) has shown that the action of emulsin on raffinose gives galactose and cane-sugar (which does not give the monose reactions), this decomposition thus occurring at the opposite end of the molecule. This observation supports Herzfeld's hypothesis that in the beet raffinose is formed from saccharose and galactose, the latter originating in the decomposition of pectic substances, possibly by the action of an anti-emulsin.

In presence of saccharose and invert sugar, raffinose may be determined quantitatively by the optical method previously described (Saccharimetry), or by the method devised by Ofner (1907), who extracts the whole of the raffinose with pure methyl alcohol, evaporates the alcohol, hydrolyses the remaining syrup for 3 hours on the water-bath with 3 per cent. sulphuric acid, and then precipitates the galactose as methylphenylhydrazone, which is quite insoluble and can be easily weighed; the corresponding weight of raffinose can then be calculated. An exact determination of raffinose in sugar, which almost always contains less than 0·5 per cent. of it, is very difficult. The presence of raffinose in small proportion in saccharose is regarded as probable if the ratio between *non-sugar* and ash is less than 1·5.

D. TETROSES

MANNOTETROSE, $C_{24}H_{42}O_{21}$, is found in manna, and yields 2 mols. galactose, 1 of fructose, and 1 of glucose on hydrolysis.

E. HIGHER POLYOSES

Starch, Dextrin, Gum, Glycogen, Cellulose

These are not, or but slightly, sweet, and are amorphous and, in some cases, insoluble in water. On hydrolysis they usually give either pentoses alone or hexoses alone, pentoses and hexoses being formed together only in rare instances. Their molecular weights are unknown, but their molecules are very large and are represented by the general formula, $n\,(C_6H_{12}O_6) - (n - 1)\,H_2O$; where n is very large, this approximates to $(C_6H_{10}O_5)^n$, which represents the results of analysis.

STARCH, $(C_6H_{10}O_5)_x$. It has already been pointed out (pp. 133, 140, and 525) how starch originates in vegetable organisms and how it passes from the leaves, where it is formed under the influence of chlorophyll and of light, to the reserve stores of the plants (tubers, seeds, etc.; in cryptogams, which have no chlorophyll, starch is not formed). It is a carbohydrate, and occurs in white granules insoluble in both cold and hot water, although with the latter it swells up, forming *starch paste*, which is coloured a characteristic deep blue

by dilute iodine solution. Starch paste is dissolved by acids, forming glucose (*see* p. 532), and by diastase (*see* pp. 133, 140, and 201), forming intermediate polyoses with less complex molecules (dextrins) and then maltose and iso-maltose. Starch does not give the reactions of the monoses (*i.e.*, with Fehling's solution, phenylhydrazine, etc.), and hence contains no free carbonyl groups, so that its rational formula (*see* pp. 523, 538) will be: $(C_6H_{10}O_5 \cdot O)$ . . . $(C_6H_{10}O_4 \cdot O \cdot C_6H_{10}O_4)$ . . . $(O \cdot C_6H_{10}O_5)$, where there is only one dicarbonyl linking, possibly in the middle; two such linkings are inadmissible, since otherwise decomposition should give, together with *d*-glucose, another substance with two carbonyl groups. Such a substance has, however, never been obtained.

The molecular weight has not been established, but it must be very high, and, according to Syniewski, the formula is $C_{216}H_{360}O_{180}$, the molecule consisting of twelve C_{18} nuclei.

The shape of the starch granules varies with the plant from which they are obtained, so that it is possible to ascertain the origin of starch by observing it under the microscope (with a magnification of 200 diameters; *see* Figs. 378 to 385).[1] When examined in polarised light, between crossed nicols, potato-starch granules, having a stratified structure and an eccentric nucleus, show a black cross like the multiplication sign (X) (Fig. 386), while other stratified starch granules with a central nucleus also behave like doubly refracting crystals but show a black cross more like the sign of addition (+); this is seen well with wheat starch (Fig. 387). Starch granules show their stratification better under the microscope if they are treated with a dilute solution of chromic acid containing a little sulphuric acid, and in some cases dark radial striæ also appear.

Commercially the name *flour* is given to starches from cereals, leguminoseæ, acorns, chestnuts, etc., and that of *starch* to those from potatoes, manioc root, arrowroot, palm stems, sago, etc., but chemically there is no difference. The flour of these plants contains more or less gluten (wheat, 12 per cent.; rice, 3 to 5 per cent.), and wheat yields 55 to 65 per cent. of starch; maize, 60 to 65 per cent.; rice, 70 to 73 per cent.; rye, 45 per cent.; oats, 32 per cent.; barley, 38 per cent.; beans, peas, and lentils, about 38 per cent.[2]

[1] Starches of different kinds may possess granules of similar form, but may be distinguished by the varying mean magnitudes of the granules, although in most kinds there are a greater or less number of granules much smaller than the average, these being sometimes grouped together in ovoid or bunch-like masses (*e.g.*, rice, oat, starch, etc.). The average sizes of the granules of the different starches, in micromillimetres (μ), are generally as follows:

(1) Wheat: large granules, 26–29μ, more common; small granules, 7μ
(2) Barley: „ „ 20μ, „ „ „ „ 4·5μ
(3) Rye: „ „ 36μ, „ „ „ „ 6μ
(4) Potato: „ „ 60–80μ, „ „ „ „ 20μ
(5) Rice: bunches, 20μ, of several granules; separate granules, 5μ
(6) Oats: „ 30μ, „ „ „ „ 8μ
(7) Maize: large granules, 18–20μ, more common; small granules, 5μ
(8) Buckwheat: „ „ 9μ (polyhedra) „ „ 5μ

[2] The mean percentage compositions of potatoes, wheat, and rice are as follow:

	Water.	Starch	Non-nitrogenous extractives	Cellulose	Fat	Proteins	Ash
Potatoes	76	18·7	1	0·8	0·2	2·1	1·2
Wheat	13·5	64	3·8	2·5	2·0	12·5	1·7
Rice	13·1	76·8		0·6	0·6	7·8	1·0

Potato starch in particular always contains, as a component resisting elimination by any purification, 0·165 per cent. of P_2O_5, corresponding with 0·35 per cent. of ash, and it has been suggested that starch consists of the molecular complex, $(C_6H_{10}O_5)n.PO\left\langle\begin{matrix}OH\\ O\\ O\end{matrix}\right\rangle Ca$, n being 260.

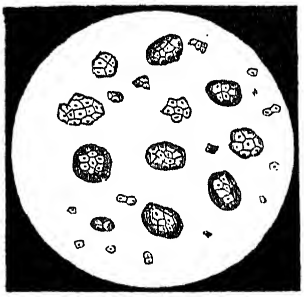


FIG. 378.—Rice starch.

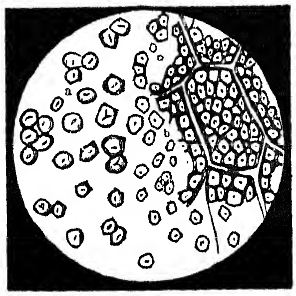


FIG. 379.—Maize starch. (a) Free granules; (b) horny part.

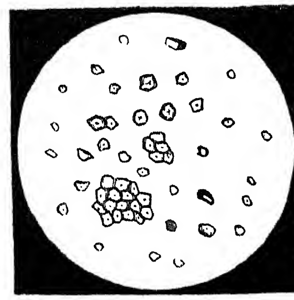


FIG. 380.—Buckwheat starch.

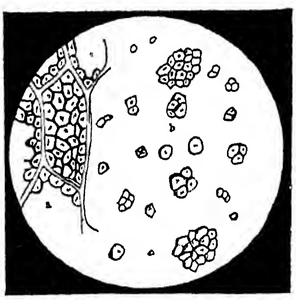


FIG. 381.—Oat starch. (a) Cellular tissue; (b) free granules.

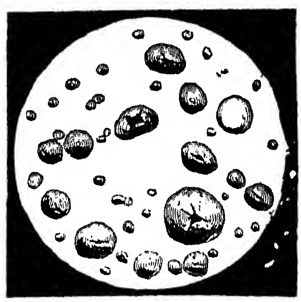


FIG. 382.—Rye starch.

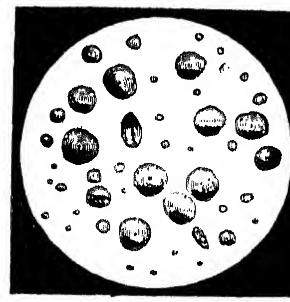


FIG. 383.—Wheat starch.

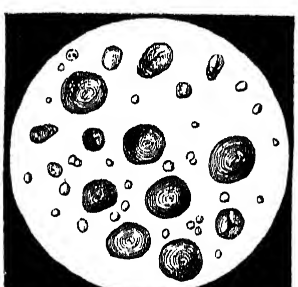


FIG. 384.—Barley starch.

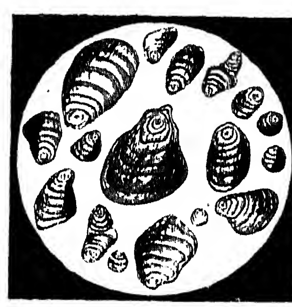


FIG. 385.—Potato starch.

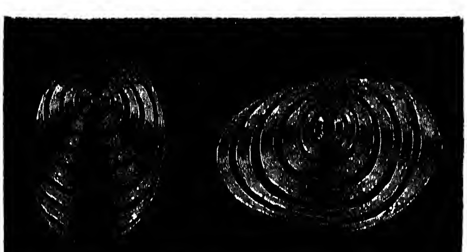


FIG. 386.—Potato starch in polarised light.

FIG. 387.—Wheat starch in polarised light.

The specific gravity of potato starch, when air-dried, is 1·5029, and when dried at 100°, 1·6330.

When heated above 160° it is transformed into dextrin.

MANUFACTURE. In Italy starch is extracted principally from rice, maize, etc., but in Germany almost exclusively from potatoes. A starch factory should always have a supply of pure cold water, not very hard and free from iron.

Fresh mature potatoes contain about 20 per cent. of starch (minimum 18 per cent., maximum 21 per cent.), the proportion being determined sufficiently exactly by a very rapid physical process, proposed in 1837 by Berg, applied in 1845 by Balling, and improved in 1880 by Behrend, Märcker, and Morgen. An exact relation exists between the specific gravity of potatoes and their starch-content, and it has been found that the difference

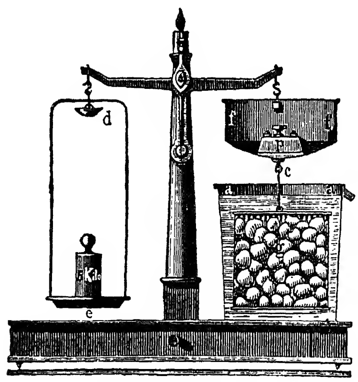


FIG. 388.

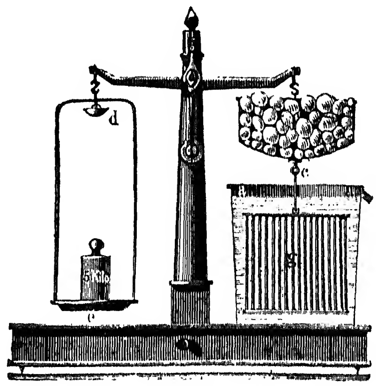


FIG. 389.

between the total dry substance (S) and the starch-content (F) is constant (the proportion of *non-starch*, N, is on the average 5·752 per cent.). Thus a determination of the dry matter gives the proportion of starch, since $F = S - N$. Further, if the relation between F and the specific gravity is determined once for all, a Table[1] can be prepared showing the proportion of dry matter or of starch from the specific gravity, which can be determined from the loss in weight of a given weight of potatoes in air (5 kilos) when weighed immersed in water; if, for instance, this weight is 400 grms., the loss of weight will be 4600 grms.

1

Weight in water of 5 kilos of potatoes, grms.	Specific gravity	Dry matter, per cent.	Starch, per cent.	Weight in water of 5 kilos of potatoes, grms.	Specific gravity	Dry matter, per cent.	Starch, per cent.	Weight in water of 5 kilos of potatoes, grms.	Specific gravity	Dry matter, per cent.	Starch, per cent.
375	1·080	19·7	13·9	480	1·106	25·2	19·4	585	1·132	30·8	25·0
380	1·081	19·9	14·1	485	1·107	25·5	19·7	590	1·134	31·3	25·5
385	1·083	20·3	14·5	490	1·109	25·9	20·1	595	1·135	31·5	25·7
390	1·084	20·5	14·7	495	1·110	26·1	20·3	600	1·136	31·7	25·9
395	1·086	20·9	15·1	500	1·111	26·3	20·5	605	1·138	32·1	26·3
400	1·087	21·2	15·4	505	1·112	26·5	20·7	610	1·139	32·3	26·5
405	1·088	21·4	15·6	510	1·113	26·7	20·9	615	1·140	32·5	26·7
410	1·089	21·6	15·8	515	1·114	26·9	21·1	620	1·142	33·0	27·2
415	1·091	22·0	16·2	520	1·115	27·2	21·4	625	1·143	33·2	27·4
420	1·092	22·2	16·4	525	1·117	27·6	21·8	630	1·144	33·4	27·6
425	1·093	22·4	16·6	530	1·119	28·0	22·2	635	1·146	33·8	28·0
430	1·094	22·7	16·9	535	1·120	28·3	22·5	640	1·147	34·1	28·3
435	1·095	22·9	17·1	540	1·121	28·5	22·7	645	1·148	34·3	28·5
440	1·097	23·3	17·5	545	1·123	28·9	23·1	650	1·149	34·5	28·7
445	1·098	23·5	17·7	550	1·124	29·1	23·3	655	1·151	34·9	29·1
450	1·099	23·7	17·9	555	1·125	29·3	23·5	660	1·152	35·1	29·3
455	1·100	24·0	18·2	560	1·126	29·5	23·7	665	1·153	35·4	29·6
460	1·101	24·2	18·4	565	1·127	29·8	24·0	670	1·155	35·8	30·0
465	1·102	24·4	18·6	570	1·129	30·2	24·4	675	1·156	36·0	30·2
470	1·104	24·8	19·0	575	1·130	30·4	24·6	680	1·157	36·2	30·4
475	1·105	25·0	19·2	580	1·131	30·6	24·8	685	1·159	36·6	30·8

and the specific gravity 5000 : 4600 = 1·087, which the Table shows to correspond with 21·2 per cent. of dry matter and 15·4 per cent. of starch. By means of the balance shown in Figs. 388 and 389 or of the Reimann or Schwarzer basket steelyard the potatoes can be rapidly weighed in air and in water at 17·5°. To calculate the practical yield the value

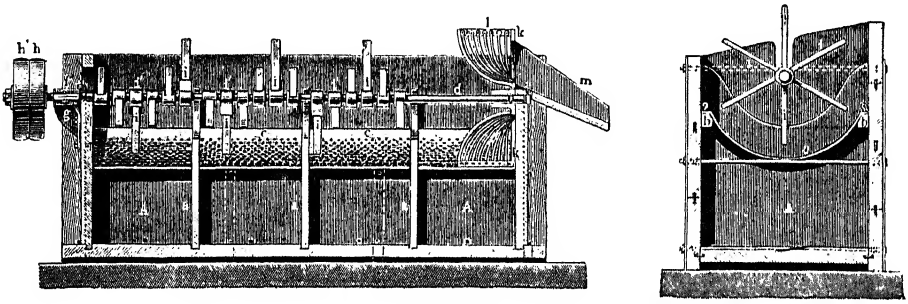
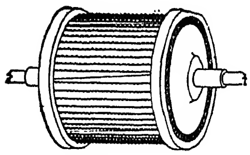
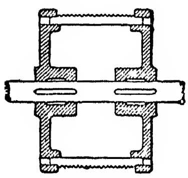


FIG. 390.





FIGS. 391 AND 392.

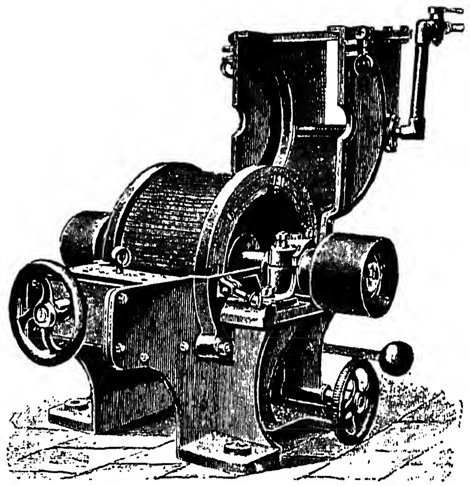


FIG. 393.

given in the Table should be diminished by 1·5 per cent., since part of the starch is converted, during extraction, into soluble sugar, which may also exist to a small extent in potatoes which are either not too ripe or too old. The washing of potatoes in starch factories is *most* important, and is carried out in machines of various types. The first washing, to remove the soil and stones, which are present to the extent of about 8 per cent., can be done in the machine shown in Fig. 105 (p. 142) or in transporter channels like those used for sugar-beets (*see* Figs. 318–320). The potatoes are then raised by an inclined Archimedean screw in a perforated channel (*see* Fig. 321), the washing being repeated with copious jets of water in a long vessel having a concave perforated bottom and fitted with vaned stirrers, which are sometimes furnished with brushes (Siemen's washer, Fig. 390). The potatoes pass along the vessel in the opposite direction to that taken by the water, which is introduced clean at the extremity where the washed potatoes emerge. The washing of 40 tons of potatoes per 24 hours requires, on an average, 20 cu. metres of water per hour.

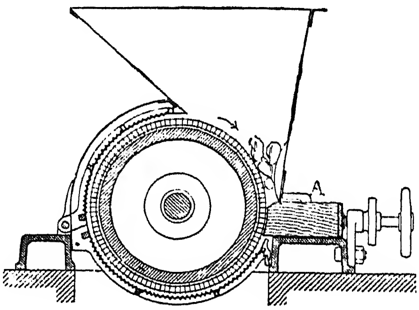


FIG. 394.

The *rasps* used to convert the potatoes into pulp, by rupturing all the starch-containing

cells, consist of a number of saw-edged steel plates fixed radially round a drum which has a diameter of 50 to 60 cm. (Figs. 391 and 392) and rotates at a speed of 800 to 1000 revolutions per minute. The Angele rasp (Fig. 393) consists of such a drum working in a cylindrical casing, which in some forms has a saw-toothed inner surface (Schmidt rasp, Fig. 394),

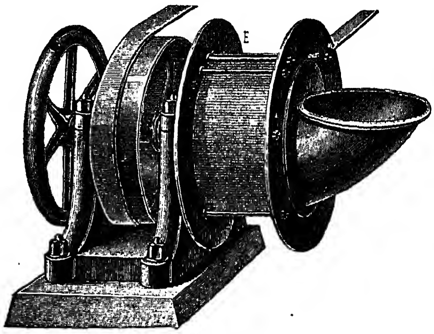


FIG. 395.

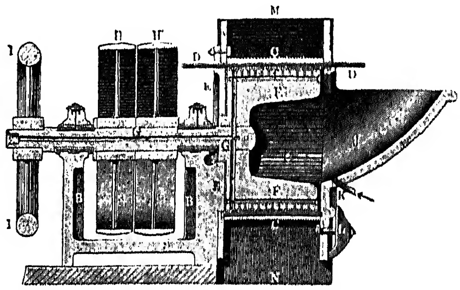
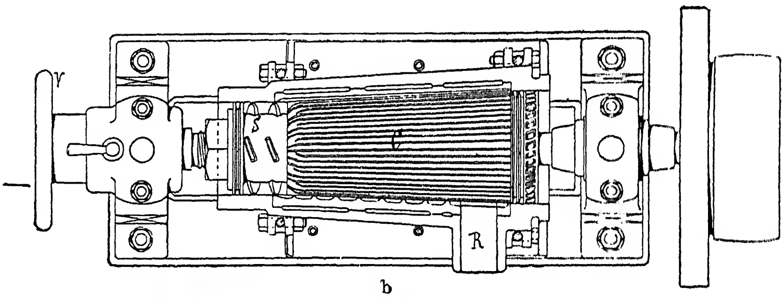


FIG. 396.



b

FIG. 397.

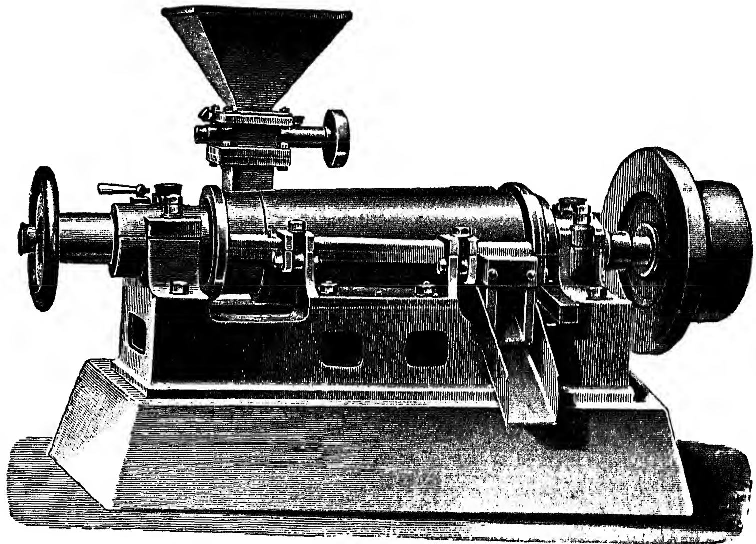


FIG. 398.

the potatoes from the feeder being forced against the drum by means of an adjustable wooden compressor, *A*, and the resulting pulp drawn between the two indented surfaces. A powerful water-jet keeps the saw-edges clean and washes the pulp into a tank underneath. The pulp from which the starch has been removed (100 tons of potatoes give 3 to 4 tons of dried residues) still contains unaltered starch cells, and as a loss of 2 to 3 per cent.

of starch would thus result, the pulp is passed into ordinary horizontal stone mills like those used in flour-mills, the stones having a diameter of about a metre and making 150 turns per minute. The Champonnois rasp, used in France, is composed of a drum, *E* (Figs. 395 and 396), formed of a number of saw-blades with the teeth turned inwards; the washed potatoes enter by the feeder, *J*, and are forced against the saw-edged periphery by the blades, *F*, which are rapidly rotated by the pulley, *H*. A water-jet supplied at *K* washes the pulp between the saw-blades into the vessel, *N*, below, loss by spurting being prevented by the casing, *M*.

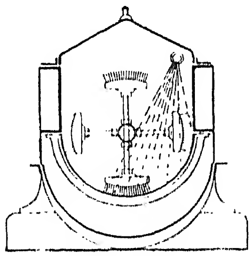


FIG. 399.

For large factories, however, Uhland has suggested the replacement of the mill by a special machine which completely disintegrates the remaining starch-containing cells without rupturing the fibres. This machine consists of a horizontal cone of cast-iron, either channelled or edged (Figs. 397 and 398) and enclosed in a casing of similar shape; by means of a screw regulator, *V*, the distance between the cone and casing can be varied. The coarse paste is introduced by a hopper and fed on to the cone, *C*, by the blades, *S*, being subsequently discharged through the channel, *R*.

In order to separate the starch granules from the residual pulp, which holds in solution the vegetable juice and in suspension the cellular residues of the vegetable tissues, epidermis, etc., the pulp is passed immediately (to avoid fermentation) on to copper sieves of various types (usually semi-cylindrical and several metres in length); these retain the residues, while a water-spray, helped by suitable scrapers, carries the starch granules through the meshes (*see* transverse section, Fig. 399); the same scrapers, which are arranged helically, carry the exhausted residues to the far end of the sieve and keep the latter clean.

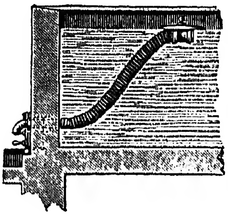


FIG. 400.

When these operations are carried out properly and in large works, the total loss is not more than 0·3 kilo of dry starch on 100 kilos of washed potatoes; these losses are detected by estimating chemically the starch in the ultimate exhausted residues.

The milky liquid collected under the sieves also contains, in addition to starch, small proportions of colouring and gummy matters, proteins, dextrin, and very fine particles of epidermis, sand, etc. In order to separate these impurities, the starch-milk is introduced into large concrete vessels, where the sand separates in a few minutes. The liquid with the suspended starch is then removed to another vessel, where the whole of the starch separates after a rest of 10 to 12 hours, but in some cases the starch is subjected to levigation with a gentle current of water in a number of vessels, in which the starch forms successive deposits. The water and the dissolved impurities are readily separated, either during or after standing, by means of a floating syphon consisting of a funnel joined to an india-rubber tube (Fig. 400). The volume of the deposit tanks is taken to be about 1 cu. metre per 100 kilos of potatoes treated.

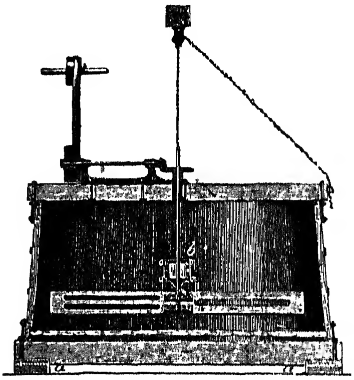


FIG. 401.

In some starch factories the starch is still separated from the milky liquid by a kind of levigation on inclined planes, the liquid passing slowly along large wooden or cement channels, 30 metres long, 1 to 3 metres wide, 50 to 60 cm. deep, and with a slope of 3 to 5 mm. per metre. The coarser starch, together with a little sand, is deposited in the first parts of the channel; then comes the best starch, while the smallest granules, mixed with a few organic impurities, are the last to settle. The water which emerges from the end of the channel is passed through two or three depositing tanks before being rejected. In order that the working may be continuous, two channels are always employed, one being in use while the starch is being removed from the other. The channels are fed from large reservoirs provided with stirrers so that the density of the starch suspension may be kept constant and uniform (3° Bé., the liquid

being fed at the rate of 6 litres per minute per 2·5 sq. metres of channel surface). The crude starch from the first and last portions of the channel may be purified by repeating the levigation, but that obtained from depositing tanks forms a compact mass composed of a lower layer of coarse granules mixed with a little sand, an intermediate purer layer, and a grey uppermost layer mixed with organic detritus. It is indispensable to wash the starch quickly, as in time the impurities impart to it a pale yellow colour. For this purpose the layer of starch—the so-called *green starch* (*i.e.*, impure, moist starch) is covered with double its depth of water, a suspended stirrer fitted with long blades (Fig. 401) being then lowered to the surface of the starch; the first more impure layer is thus stirred up so as to form a dense milk of 4° to 5° Bé., this being deposited in an adjacent wooden vat or on the inclined channel. The middle purer layer is then stirred up and the suspension removed, and so on.

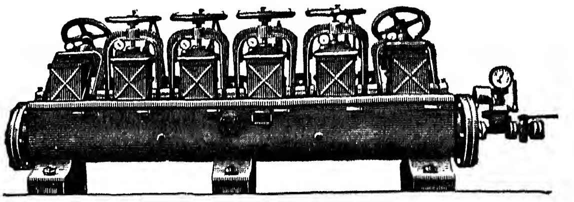


FIG. 402.

In these wooden vats (*see* Fig. 401) the stirring is repeated, this operation being continued until a perfectly white starch is obtained, the wash-waters being removed after each deposition.

When the starch is not refined in this way and dried, the growth of mould is prevented by keeping it under water slightly acidified with sulphuric acid until it is to be sold. This green starch, which is used, for example, for manufacturing glucose, contains about 50 to 55 per cent. of water; part of this can be removed in centrifuges similar to those used for sugar (p. 565), the perforated drum being coated inside with a fine cloth to retain the granules. The superficial layer of the cake of starch is scraped off, as it contains impurities, and the remainder (with 35 to 40 per cent. of moisture) then discharged below; with a drum 80 cm. in diameter 50 kilos of starch are obtained. The centrifuges are fed with a dense suspension of the starch of 20° Bé. The impure grey starch obtained in the secondary sedimentation vessels is mixed to a dense milk and passed through fine silk sieves, which

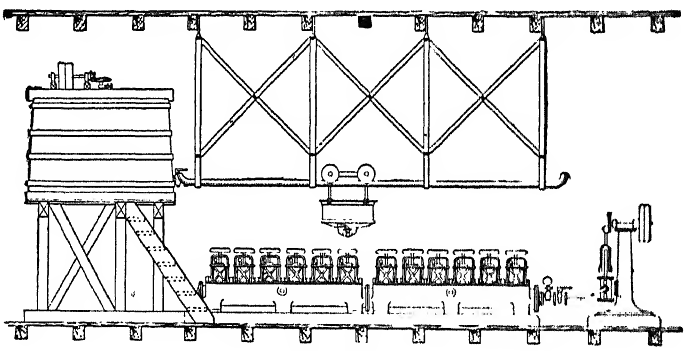


FIG. 403.

retain the detritus and solid proteins, etc., the sieved milk being conveyed to other finer sieves and then to the inclined channels or sedimentation vats. To prevent bacterial action and to increase the whiteness of starch, 0·5 kilo or more of calcium bisulphite solution (in some cases sulphurous acid is used) is sometimes added to each cubic metre of the milk. These reagents, as well as sulphuric acid or caustic soda in small proportions, facilitate the deposition of the starch in the tanks, but they impart a faint reaction to the final starch, and it is advisable to employ them only in the treatment of frozen or bad potatoes, where the product readily ferments and turns yellow. Bleaching is sometimes effected with dilute, filtered calcium hypochlorite solution (1 : 300), together with sulphuric acid; after a few minutes' contact, the starch is washed in an abundant supply of cold water until the reaction of the chlorine disappears. The last trace of yellow in the starch may be corrected by slight blueing with ultramarine, indigo carmine, Prussian blue, etc.

When potato or cereal starch is to be prepared in cubical or similar cakes, the mass

from the sedimentation tanks is introduced into moulds of galvanised or tinned iron with perforated bases (the cubes are 16 cm. in each direction); these are either enclosed in evacuated cases or, as Uhland suggested, subjected to considerable air-pressure, so as to remove the water as far as possible (*see* Fig. 402). Fig. 403 shows how the batteries of moulds are arranged in large factories; the dense starch-cream from the vat fills a hopper travelling on a suspended iron rail and stopping above each mould to fill it; when all the moulds are full, they are closed hermetically and the air-compressor started. With a suitable machine the smooth cakes are removed whole from the moulds, and as they contain very little water, the time required for drying is considerably shortened.

Modern plants make use of another arrangement devised by Uhland (Fig. 404). Here the moulds are fitted inside with a rubber bag with a perforated base and covered with cloth; this fits closely to the walls and gives a purer starch, while the moulds can be thoroughly cleaned after each operation.

The *drying* of the starch is carried out in hot-air desiccators, which readily reduce the moisture to 20 per cent., which is the customary proportion; if more moisture is present an allowance is made to the purchaser, but if there is less than 20 per cent. the seller loses, as no allowance is then made. In order to obtain starch of good appearance the temperature of drying should be about 30° to 35° (at 50° it begins to swell and form lumps) and the air should issue from the desiccator almost saturated with moisture after traversing all the frames or gratings on which the moist starch is spread in a thin layer or in cakes. The best arrangement consists of channels or galleries 10 to 12 metres long, 1·2 metre wide, and 2 metres high, through which trolleys carrying the frames pass from one end to the other; the hot, dry air is injected under slight pressure in the opposite direction by a large helical fan, gentle suction being applied at the far end if necessary. Rapid drying depends not so much on the temperature as on the supply of the proper amount of pure, dry air. The doors of the drying tunnel slide up, and are opened just sufficiently to allow of the entry and exit of the trolleys from time to time (every hour).

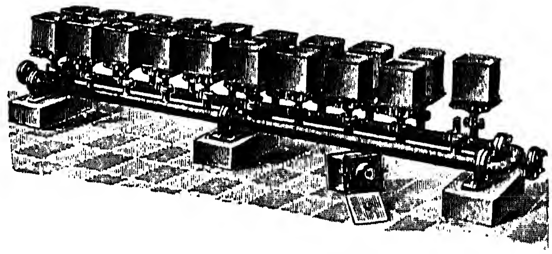


FIG. 404.

It has recently been proposed to employ mechanical driers consisting of a number of stories fitted with endless bands, or of long revolving cylinders, while in some cases drying in a vacuum has been practised as with distillery residues (*see* Fig. 151, p. 183), time and space being thus economised and the output consequently greatly increased.

The dried starch forms friable lumps, and to obtain it in powder it is passed first into grooved cylinders and then into sieves similar to those employed in mills. For the use of ball-mills, *see* Vol. I., p. 652; this Vol., p. 269. Microscopical appearance, *see* p. 587.

Yield of Starch and Treatment of Residues. Of 20 kilos of starch present in potatoes, 17 to 18 are usually obtained in the pure, dry state, the rest going into the residues. The moist pulp, freed from starch (within 0·5 per cent.), contains the parenchyma and epidermis of the potatoes, which are composed largely of cellulose saturated with aqueous juices. The pressed pulp (about 16 per cent. of the weight of the potatoes), which is sometimes dried (it then constitutes 3 to 4 per cent. of the weight of the potatoes and contains 50 to 60 per cent. of starch), forms a good cattle-food, either alone or mixed with bran, chaff, etc. It is dried in the vacuum apparatus used for "grains" (*see* p. 183) or for beet-pulp (*see* Fig. 335, p. 553). The waste waters contain potash salts (0·06 per cent. K_2O + 0·017 per cent. P_2O_5 + 0·1 per cent. ash + 0·24 per cent. sugar + 0·12 per cent. gum + 0·17 per cent. nitrogenous substances) and may be used for irrigating pasture land; if it is not digested quickly it undergoes fermentation. These waters are readily clarified by colloidal aluminium hydroxide. The moist, non-pressed pulp has the following percentage composition: water, 86; protein, 0·7 to 0·9; fat, 0·1; starch and extractives, 11·2; cellulose 1·5; ash, 0·4.

WHEAT STARCH. Since wheat also contains, in addition to 56 to 65 per cent. of starch, 12 to 16 per cent. of gluten, the separation of the latter renders the preparation of the starch more difficult. By the fermentation process (Halle) the gluten is rendered soluble

and consequently lost, so that only wheats containing little gluten are treated in this manner. The non-fermentation process, in which the gluten is recovered, is the one usually employed, more especially because no large amount of bad-smelling liquor is formed, as is the case with the other method.

In the fermentation process the wheat is cleaned and steeped in water in apparatus similar to that used with barley to be malted (*see* Fig. 155, p. 195). When sufficiently soft to be squeezed between the fingers, the wheat is passed between a pair of smooth rolls which break the epidermis without crushing it too much. The mass is placed in large tanks and covered with the acid liquid from a previous fermentation, alcoholic fermentation starting in a few days and being followed by acid fermentations (lactic, butyric, acetic, etc.) with evolution of gas; the fermentation is complete in 10 or 12 days in summer or 20 days in winter, the liquid being then clear, yellow, and covered with mould, but not yet smelling. The acid liquid is decanted off, and the starch separated from the bran in a finely perforated drum under a current of water. The solid residue serves as cattle-food, while the starch-milk is allowed to deposit in the ordinary vats, where it is washed; it is then conveyed to the fine sieves and inclined channels (*see under* Potato Starch). The pure starch separated in this way should, however, contain a small proportion of gluten, since, during the drying, this facilitates the formation of so-called crystals desirable in the commercial product.

The crude starch-milk can be purified more rapidly in the Fesca-Decastro centrifuge, which has a non-perforated drum. The purer starch is deposited first in a compact layer on the inner surface of the basket and the less pure starch-milk remaining is discharged automatically before it deposits its impurities, new starch-milk being introduced and treated similarly until a thick layer of moderately pure starch is obtained. The centrifuge is stopped, the water discharged from the middle, and the yellowish, superficial portion of the starch, which contains gluten, etc., removed with a sponge. The starch is then discharged, mixed with water in a vat fitted with a stirring arrangement, and the starch-cream, sometimes after a little ultramarine or indigo carmine has been added, introduced into the suction moulds.

The drying of the cakes (*see* Potato Starch) is carried out *immediately* (to avoid mould-growth), and in winter-time this is done in an oven, the temperature of which is raised from 30° to 75°; in the summer the drying is begun in the air. When a certain stage is reached in the drying process, the cakes shrivel at the surface; this less pure portion is removed and the cakes broken into smaller blocks, which are wrapped in paper and dried further. Under this treatment the mass gradually assumes the radiating structure.[1]

In the *non-fermentation process* the crushed wheat is treated with a stream of water, being manipulated meanwhile in the form of a paste, which is placed on perforated channels or sieves so that the whole of the starch is gradually removed and the pasty gluten left. The starch is then deposited in the ordinary manner, while the gluten is transferred to rotating cylinders with their inner surfaces covered with points, which retain the *pure* gluten;[2] the bran is washed away with water.

According to a suggestion by Fesca, the dry ground wheat is mixed with water and the paste introduced into a centrifuge with a perforated drum, the starch being separated by a continuous current of water, while the gluten remains in the centrifuge; the further operations are as usual. The Fesca process is very simple and more convenient than that

[1] *Wheat flour* attains its maximum whiteness 30 to 60 days after grinding and retains it until about the sixth month, after which it slowly darkens. In America various patents have been filed, during the last few years, for obtaining this maximum whiteness more rapidly by treating the flour with ozone, chlorine, bromine, sulphur dioxide, etc., but better results are obtained with nitrogen peroxide (NO_2). According to some observers, flours bleached in this way begin to darken earlier, irregular staining taking place. The process which has given the most favourable results and has been largely applied in America and before the War also in Italy, is that of Wesener (Ger. Pats. 209,550 and 232,204), according to which flour is bleached instantaneously in contact with a current of air containing mere traces of nitrosyl chloride (*see* Vol. I., p. 380); 1 kilo of the latter is sufficient to bleach 100 tons or even more of flour.

[2] In presence of a little water and at a moderate temperature, the *gluten* thus obtained undergoes a slight fermentation and becomes liquid; when dried in thin layers on metal plates, this is obtained in transparent sheets, which are used as a glue in the manufacture of boots. Or the gluten is mixed with 5 per cent. of powdered salt and made into strings in presses; the strings are dried in an oven, when they become friable and readily convertible into flour, which is used in the preparation of dough and serves as a foodstuff when mixed with other products. The gluten contains 75 per cent. of nitrogenous substances, 21 of non-nitrogenous substances, 1 to 5 of fat and 1·5 of ash.

described above. The average yields, calculated as percentages on the wheat, are as follow: first quality starch, air-dried, 54; gluten flour, 12; bran, mixed with a little gluten and starch, 19·5; matters dissolved in the waste water, 14.

Microscopical appearance, *see* p. 587.

RICE STARCH. On the average, rice[1] contains 77 per cent. of starch and less gluten (4 to 5 per cent.) than wheat, but the starch is more difficult to separate (for 1 part of gluten about 1 part of starch is lost). Of all the processes which have been suggested, that devised by Orlando Jones in 1840 still gives the best results. Use is generally made of waste rice (broken rice, costing 14*s.* to 24*s.* per quintal according to the season), which is softened in a large galvanised iron or iron steeping cylinder with a conical base, by means of dilute solutions of caustic soda (0·3 per cent. in winter, 0·5 per cent. in summer). Here it is left for 5 to 15 hours, being mixed every 3 to 5 hours with a vigorous air-jet; in winter the alkali solution is heated to 20°. The duration of the steeping varies with the quality of the rice and with the season of the year; Italian rice requires 5 to 6 hours and Rangoon rice as much as 14 hours, the soda solution being changed in the latter case after six or eight hours. After steeping, the rice can be readily crushed between the fingers. The dissolved gluten (20 to 30 grms. per litre) is separated from the alkaline liquid simply by acidification with sulphuric acid (in order to bring the gluten into such a condition that it can be filtered in a filter-press, the temperature is raised to 80° or 1 kilo of lime is added per cubic metre of the alkaline solution). In some cases the gluten is extracted with an alkaline liquid in an apparatus similar to beet-diffusors (*see* p. 572), while in others the extraction is carried out in a vacuum with agitation. The swollen and softened rice, containing a little of the alkaline solution, is then ground between horizontal millstones, a liquid paste with 22 to 26 per cent. of starchy matter being obtained; this is pumped up into large *square* cement tanks provided with stirrers (*see* Fig. 401), where it is treated with more dilute caustic soda solution (0·2 per cent.), care being taken in summer that the temperature does not rise sufficiently to admit of fermentation. In these tanks the separation of the starch from the liquid occupies about $1\frac{1}{2}$ hours after the stirring is stopped. The liquid is decanted and the residual starch mixed with a fresh quantity of 0·2 per cent. NaOH solution and left for 45 minutes to settle. In some cases this washing is repeated a third and fourth time, the thin surface layer of yellow starch containing gluten, etc., being scraped off each time before adding fresh washing water; the scrapings from the first and second settlings are ground again in the stone mill, sieved, and mixed with the other starch. After the final washing, for which water is used, the starch-milk is conveyed to other cement depositing tanks, being previously passed through oscillating, inclined silk sieves or through revolving perforated cylinders sprayed outside with water to prevent obstruction by impurities or by solid gluten (the gluten separates best with rather hard,

[1] *Rice* (*Oryza sativa*) is an annual plant belonging to the Gramineæ indigenous to Eastern India and, according to some, to Ethiopia. In Europe it is cultivated principally in Italy and also in Spain and in the south of Russia, particularly on irrigable lands. In Japan and Brazil it is grown in the moist soil of warm, rainy regions, while in America it is extensively cultivated in Florida and Southern Carolina. In rice-plantations the bottom of the plant is kept under almost stagnant water, and, on account of the miasmata, which cause malaria, the fields should be at some distance from any habitation; the ripening of the head is brought about by the intense heat of summer. After the harvest the rice is separated from the ear by means of suitable machines (threshers), but still retains the glumes or husk, being known as *paddy rice*. This is separated from the residues by means of concentric toothed cylinders and is then sieved and placed between two light, horizontal, stone discs (or *brahmin*), one of which is fixed while the other revolves; in this way the husk is removed. The husk was formerly, and to some extent is now, separated from the rice by means of vertical pestles, which fall automatically but without touching the bottom of the mortar filled with the rice; the grains of rice are thus rubbed, one against the other, and the husk removed. The complete removal of the husk and dust is effected by means of a simple vertical mill similar to the double one used for black powder (Fig. 185) and making 30 to 40 turns per minute. The rice is finally polished in a double vertical conical apparatus, the inner cone of which is provided with brushes of vertical metal wires and revolves at the rate of 200 turns per minute, and rubs the rice against the outer perforated cone; the polished rice is discharged at the bottom. 100 kilos of paddy rice give 77 kilos of dehusked rice, or 67 of commercial rice, or 63 of unpolished or partially polished rice, or 59 of polished rice. The residues consist of about 1·5 per cent. of waste, 20 per cent. of husk, 2·5 per cent. of resin, and 8·5 per cent. of meal, which is used as fodder, and contains, on an average, 12·5 per cent. of fat, 13 per cent. of total protein, 5 per cent. of cellulose, 45 per cent. of extractives, and 8 per cent. of ash. A hectare of good rice land yields 60 to 70 hectols. of rice. The following prices were quoted for rice in October, 1911: Paddy rice: Ostiglia, 17*s.* 6*d.*; Japanese, 13*s.* 6*d.*; Burmese, 15*s.* per quintal; Ostiglia rice, first quality, 36*s.* 10*d.*, third quality, 34*s.*; Burmese, 28*s.*; first quality Japanese, 26*s.* 6*d.*

chalky water). The deposited starch is mixed with water and centrifuged in a non-perforated drum in the manner employed for wheat starch, the yellow surface layer being removed with a sponge. Finally, it is made into a thick paste (24° Bé. or about 50 per cent. of water; alkalinity less than 0·2 per cent.) with water and moulded under an air-pressure of two atmospheres or with a suction-pump giving a vacuum of 600 mm. (*see* Figs. 402, 403, 404); the starch has not a very bright appearance if made into cakes immediately it leaves the centrifuge. In this way blocks containing 40 to 50 per cent. of water are obtained, and these are subjected to a preliminary drying in an oven at 40° to 45°; after 5 to 8 days the mass contains 30 per cent. of water and is shrivelled at the surface, owing to efflorescence of the gluten, etc. This impure, yellow portion, which may constitute 15 per cent. of the whole, is sawn off, washed, centrifuged, filter-pressed, and then either treated again or dried and sold as a lower-grade product. The remaining blocks are dried further in the air or, more commonly, after wrapping in paper, in an oven, where the temperature is raised to 25° in two days, to 28° on the third, and then slowly to 32° or 35°. In 15 to 20 days the mass contains 12 per cent. of water and is crystallised completely in long, fragile needles with irregular surfaces; these blocks are then exposed to the air (sheltered from dust), the normal moisture-content of 15 to 18 per cent. being thus acquired (the alkalinity is usually below 0·15 per cent.). According to Ger. Pat. 205,763, the formation of needles is accelerated by drying the moist starch rapidly, grinding and compressing in the moulds; the cakes are then wrapped in paper and placed in the ordinary channel ovens, through which warm, *moist* air is passed. The starch may be bleached in the ordinary way with sulphur dioxide and blued with ultramarine (about 150 to 200 grms. being added per 500 litres of dense cream before introducing it into the moulds). Difficulties are often encountered in the manufacture of rice starch, owing to the readiness with which fermentation occurs, this leading to generation of gas and to trouble in the settling and clearing of the liquids; the remedy lies in increasing the concentration of the alkali employed or in the use of sulphur dioxide. Rice gluten, separated from the various residues and alkaline wash-waters, cannot be used for making shoemaker's paste.

Rice starch is employed largely for making face powder and almost exclusively for the starching of linen, a gloss being obtained in the latter case by the addition of borax (6 to 8 per cent.), finely powdered stearic acid (2 to 3 per cent.), etc.

Statistics, *see later*. Microscopical examination, *see* p. 587.

MAIZE STARCH. The maize, which has an average starch-content of 62 to 65 per cent., is softened in tepid water for 3 or 4 days and ground coarsely, the germ and bran being then separated and the remaining flour treated several times with sulphurous acid. It is then sieved and the resulting starch-milk treated as usual in sedimentation tanks, the last portions of gluten being removed. The form of the granules is shown on p. 587.

SOLUBLE STARCH. This is used in large quantities as a dressing for textile fibres and as an adhesive. It is prepared by the action on starch at different temperatures of many different reagents, such as alcohol and water, caustic soda, sulphuric acid, calcium hypochlorite, gaseous chlorine, ammonium persulphate, hydrogen peroxide, formic acid, gaseous hydrogen chloride, *diamalt* (a dense diastase syrup or malt extract, known in Germany as *diastofor*), hydrofluosilicic acid (at 80°), etc.

USES OF STARCH. Large quantities of starch are used as a dressing in the spinning and weaving of textile fibres, in calico printing as a thickening material, in the manufacture of paper, in the preparation of adhesive paste, in the laundry and kitchen, as well as for making dextrin and glucose.[1]

DEXTRIN is found ready formed in various vegetable juices, but is always mixed with starch and sugar, while that prepared artificially from starch by the action of heat, acid, or diastase consists of a mixture of products intermediate to starch and sugar (maltose and glucose). Several dextrins of various molecular magnitudes are known (achroodextrin, amylodextrin, erythrodextrin, etc.). Biltz and Truthe (1913) determined the molecular weights of various dextrins by measuring the osmotic pressures of their solutions, use being made of artificial membranes of copper ferrocyanide enclosed in pure collodion. The

[1] The *adhesive power* of starch is determined by heating a mixture of 4 grms. with 50 c.c. of water over a naked bunsen flame and boiling for a minute until it becomes transparent and begins to form froth, the flame being then removed; if, after shaking and allowing to cool, the paste is thick and cannot be poured out, the adhesive properties are satisfactory.

values obtained were: amylodextrin, 20,500 to 22,000; achroodextrin, 8200 to 11,700; erythrodextrin, 3000 to 6800; β-dextrin, 950.

According to some, dextrin has a marked aldehydic character, and hence gives all the reactions of the monoses, including those with phenylhydrazine and Fehling's reagent, while others hold that the aldehydic character is feeble, and others, again, that Fehling's solution is not reduced, even on boiling. This diversity of view is explained by the great difficulty of separating chemical individuals from the mixtures containing them; in any case all the dextrins prepared commercially reduce Fehling's solution to a greater or less extent. Dextrin is not fermented directly, and diastase does not transform it entirely into fermentable sugar (maltose), 15 per cent. remaining unchanged, although this slowly becomes fermentable under the prolonged action of diastase (*see* p. 141).

Dextrin is known also by various commercial names (*vegetable gum, starch gum, artificial gum, gommeline, British gum, etc.*), and forms a light powder having a slight smell of new bread; it is white, yellowish, or even brownish, according to the purity, the method of preparation, and the purpose for which it is intended. It is sometimes sold in semi-transparent, yellowish lumps. It dissolves completely in water when pure and has a high rotatory power ($[\alpha]_D =$ about $194°$); it is insoluble in alcohol. With iodine solution it gives a reddish coloration, and boiling dilute hydrochloric or sulphuric acid converts it into glucose, while malt transforms it into maltose; with concentrated nitric acid it gives oxalic acid. Commercial dextrins often contain a little starch and glucose, so that they then give a violet coloration with iodine and reduce Fehling's solution in the hot; the specific rotation varies from 125° to 225°.

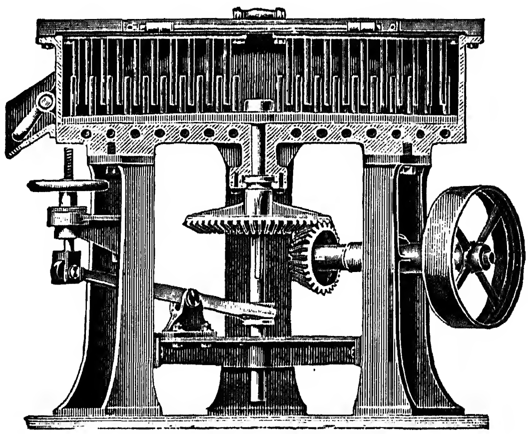


FIG. 405.

MANUFACTURE. According to the ordinary Heuse process, 1000 kilos of starch are moistened with 2 kilos of nitric acid of 40° Bé. diluted with 300 litres of water, the paste being made into loaves which are dried in the air, ground finely, and heated for about two hours at 100° to 120°. For this purpose the starch is either spread in thin layers on a number of trays, which are arranged in a suitable oven, or placed in a circular Uhland apparatus (Fig. 405), the base of which is heated with superheated steam while the mass is mixed continually by means of a stirrer fitted with a number of pegs. If the temperature is raised to 130° to 140°, the duration of heating is shortened, but yellow and not white dextrin is obtained.

Dextrinification is complete when the product is entirely soluble in water and gives no longer a blue, but only a reddish brown colour with iodine solution.

The preparation of dextrin by torrefying starch is, however, a very simple process, which can also be carried out in the Uhland apparatus, the starch being stirred and heated at 180° to 200° by means of superheated steam until it assumes a brownish yellow colour and gives the reactions just mentioned. The steam-pipes are utilised for the circulation of cold water immediately dextrinification is complete. Its moisture-content is adjusted to about 12 per cent. before it is marketed.

To distinguish commercial dextrins from gum arabic, the aqueous solution is treated with either oxalic acid or ferric chloride in the cold or concentrated nitric acid in the hot: dextrin is not altered in this way but the gum becomes turbid or gelatinises. Further, dextrins are strongly dextro-rotatory, while gums are almost always lævo-rotatory.

GUMS. These are also polyoses $(C_6H_{10}O_5)_x$, which are frequently formed in plants and are soluble in water or swell up, giving viscous, sticky liquids; they are insoluble in alcohol and other solvents of the resins. **Gum Arabic** is excreted, from December to May, as an adhesive juice from the bark or, better, from the roots of certain African acacias, 3 to 5 metres in height; after drying, it has the sp. gr. 1·487, and the various components yield *d*-glucose and arabinose on hydrolysis. In Egypt these acacias occupy entire forests, especially in the provinces of Kordofan and Gedda (White Nile). The natives make a number of incisions in the roots, and the liquid which issues condenses in the air into nutlike masses, these being detached before the commencement of the rainy season. The grains have the colour of amber and become white when exposed to the air, so that there are two qualities of the gum. It is used in large quantities by pastrycooks and in textile dyeing and printing, and generally as an adhesive.

A similar type of gum, obtained in abundance from Senegal, issues from certain wounds of cherry- and peach-trees, while **Gum Tragacanth** is extracted from certain varieties of *Astragalus* in Serbia, Syria, Persia, etc., and, after being rendered mucilaginous by prolonged contact with water, is used as a thickening material in calico printing, etc.

The value of a gum is ascertained by determining the viscosity of its solution (*see* p. 91).

GLYCOGEN or **Animal Starch** is also a polyose $(C_6H_{10}O_5)_n$, found principally in the blood and liver of mammals. It is a white amorphous powder insoluble in cold water, and is coloured reddish violet by iodine solution. It is converted into maltose by an enzyme, whilst on the death of the animal containing it or on boiling with dilute acids it is transformed into *d*-glucose.

CELLULOSE, $(C_6H_{10}O_5)_n$

The actual molecular magnitude of cellulose has not yet been established but is certainly very great.[1] Like starch, it may be regarded as a multiple of $C_6H_{10}O_5$, but, while starch is able to undergo transformations (into dextrin, maltose, etc.) in the vegetable organism, cellulose represents a stable complex. Together with *lignin*, cellulose forms the principal component of the cell-walls of plants. It occurs, for instance, in wood and cotton, in different degrees of purity, while in different vegetable organisms the cells assume distinct and characteristic forms, readily recognisable under the microscope (*see* Part III., Textile Fibres). Cotton-wool and Swedish filter-paper consist of cellulose in an almost chemically pure state.[2]

Pure cellulose forms a white amorphous mass and can be obtained by treating cotton (flocks) successively with hot dilute caustic potash, hot dilute hydrochloric acid, alcohol and ether, and drying at 125° to eliminate the water with which a small part of the cellulose is hydrolysed.

[1] In order to determine at least *minimum* values for the molecular magnitudes of the polyoses, Skraup (1905) applied to these compounds a reaction given by the bioses: when the latter are treated with acetic anhydride and dry hydrogen chloride gas, they give chloracetyl-derivatives without undergoing hydrolysis, and the chlorine-contents of these derivatives indicate the molecular weights. In this manner the molecular weight of *cellulose* is found to be at least 5508, that of soluble *starch* 7440, and that of *glycogen* 16,350.

[2] From the crude cellulose or woody parts of plants, J. König (1906) separated four components giving the following reactions: (1) *hemicellulose*, which is hydrolysed by dilute mineral acids; (2) *cutin* or *suberin*, which is soluble in alkali but insoluble in ammoniacal copper oxide solution; (3) *lignin*, which is oxidisable by weak oxidising agents; (4) *true cellulose*, insoluble in dilute acid or alkali, soluble in ammoniacal copper oxide, not oxidisable by hydrogen peroxide.

The part of the cellulose which enters into the formation of the cell, but gives no glucose on hydrolysis, constitutes the hemicellulose group; the hemicelluloses of lupins, certain lichens, etc., give galactose, xylose, mannose, etc., on hydrolysis.

Cross and Bevan divide celluloses into four groups: (1) celluloses which are hydrolysed with difficulty and contain no active carbonyl groups (aldehydic or ketonic), the characteristic type of this group being the cellulose of cotton; (2) celluloses which contain active carbonyl and, sometimes, methoxyl groups, and give furfural when hydrolysed with hydrochloric acid; such are the celluloses of wood and straw; (3) celluloses (or *hemicelluloses*) which are easily hydrolysed; (4) complex celluloses.

The furfural and methylfurfural formed by the celluloses of group (2) may be derived from the *pentoses* yielded by the pentosans of the celluloses or from the *furfuroids* which occur in abundance in vegetable organisms, and although they contain no pentosans yet give furfural (*see* p. 528).

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Cellulose does not dissolve in ordinary solvents, but is completely soluble in concentrated zinc chloride solution, concentrated sulphuric acid, nitric acid (sp. gr. 1·52), 41 per cent. hydrochloric acid (which converts it completely into glucose in 48 hours), hydrofluoric acid, phosphoric acid, xanthic acid ($C_2H_5O \cdot CS \cdot SH$) or, best of all, in an ammoniacal solution of copper oxide (Schweitzer's reagent, prepared by dissolving freshly precipitated, well-washed copper hydroxide in concentrated ammonia solution in the proportion of CuO to $4NH_3 + 4H_2O$); from this solution it is reprecipitated as gelatinous *hydrocellulose* by acids, alkali salts, or sugar solutions. Hydrocellulose dissolves in a mixture of caustic soda and carbon disulphide, and is reprecipitated in a gelatinous state by salts, etc. These jellies are used for the manufacture of artificial silk.

Dubosc (1906) found that solutions of thiocyanates constitute good solvents for cellulose; ammonium thiocyanate, for example, gives viscous solutions from which water separates gelatinous cellulose. In dissolving in any solvent, however, cellulose generally dissociates into simpler molecular complexes, which cannot be converted into the *original cellulose* but give hydro- or oxy-cellulose, which show more marked reducing properties.[1]

The prolonged action at moderate temperatures of acids, alkalis, and enzymes results in the gradual hydrolysis of cellulose, so that, while before hydrolysis only a brown colour is obtained with iodine solution, after the action of concentrated sulphuric acid a blue reaction is given; in this reaction the cellulose swells and dissolves into a kind of paste, and the action on this of water separates substances similar to starch (*amyloids*). If the hydrolysis is carried further the reactions of the dextrins may be obtained, dilution with water and boiling then resulting in the formation of monoses (hexoses and pentoses).[2] Cellulose may hence be regarded as composed of complex anhydrides of hexoses and pentoses, and recent investigations indicate that the behaviour of cellulose is best explained by regarding it as a *colloid* containing groups with acidic hydrogen ions, others with basic hydroxyl ions and some non-dissociated groups; the reactions of cellulose with both basic and acidic substances are explainable in this way.

Cellulose has alcoholic characters, the hydrogen of each of the hydroxyl groups being replaceable by an acetyl- (*see* p. 381) or nitro-group, etc. Not more than three or four hydroxyl groups correspond with each six carbon atoms; with nitric acid three nitrate groups can be introduced, while with acetic anhydride, in presence of sulphuric acid, esters (cellulose acetates) corresponding with four hydroxyl groups per C_6 are obtainable (Cross and Bevan, 1905).

According to H. Ost (1906) the ordinary methods of acetylation always yield triacetates of cellulose, but *hydrocellulose* is first formed as an intermediate product, $(C_6H_{10}O_5)_6, H_2O$, and it is this which forms the plastic triacetate, $[C_6H_7O_5(COCH_3)_3]_n, H_2O$, used as artificial silk, etc.[3] If the action of sulphuric acid and acetic anhydride is carried too far, friable

[1] Other solvents for cellulose, as given by Denning (1911), are: concentrated aqueous solutions of $SbCl_3$, $SnCl_4$, $ZnBr_2$, best in presence of a halogenated acid; $CaCl_2$, $CaBr_2$, $BaCl_2$, $MgBr_2$, LiCl, KBr, in presence of formic acid or of formic and hydrochloric acids together. A solution of zinc chloride in concentrated hydrochloric acid dissolves cellulose more easily than aqueous zinc chloride.

[2] Numerous attempts have been made to convert wood industrially into saccharine substances and so prepare *alcohol* (*see* p. 167), but it was only in 1910–1911 that Flechsig, Ost, and Wilkening showed that cellulose can be transformed completely into fermentable glucose by dissolving it in concentrated sulphuric acid, diluting until the solution contains only 1 to 2 per cent. of acid, and then heating at 110° to 120° (but not to 125°, as was done by Simonsen, since a part of the glucose is thereby destroyed). Cohol (1912) obtained 25 per cent. of reducing substances from sawdust by heating the latter under pressure at 125° to 150° in presence of 0·5 to 0·3 per cent. of hydrochloric acid.

[3] **Cellulose Acetate** is soluble in chloroform, tetrachloroethane, aniline, pure acetic acid, epichlorhydrin, and boiling nitrobenzene. The less highly acetylated products are soluble in alcohol, giving a solution which, together with camphor, serves for the preparation of *cellite films* for cinematographs; these films are considerably less inflammable than those of celluloid. The

acetates of no industrial value are obtained, the ultimate product being a crystalline octo-acetate of a biose, *cellose* or *cellobiose* $(C_6H_{10}O_5)_2$, H_2O, which can be liberated from the acetate by hydrolysing with alcoholic potash but is of no value industrially. The rotatory power of cellobiose is 33·7°, the solubility of its phenylosazone in boiling water 1 : 135, and the melting-point of its phenylosazone 198°; it is thus quite different from maltose (rotatory power, 142·5°; melting-point of phenylosazone, 206°; solubility of phenyl-osazone in boiling water, 1 : 75). The origin of cellulose in plants cannot be regarded as a condensation of starch; the latter is probably converted into glucose, which gives cellulose on condensation. The preparation of nitrocellulose (*pyroxylin*, guncotton, collodion-cotton) has already been described in the chapter on Explosives (p. 286).

Cellulose Formate (Blumer, Ger. Pat. 179,590) has also been prepared.

At 210° cotton begins to decompose with evolution of carbon monoxide and dioxide, methyl alcohol, acetic acid, acetone, hydrocarbons, etc. (*see* Distillation of Wood, p. 330). By the dry distillation of pure cellulose (Swedish filter-paper) under ordinary pressure, Erdmann and Schaefer (1910) obtained about 5 per cent. of tar, 42 per cent. of acid liquors, and a residue of carbon, together with gas containing 66 per cent. CO, 19 per cent. CH_4, 11·5 per cent. H_2, etc.; from the acid liquors, acetone, formaldehyde, furfural, methoxy-furfural, *maltol* ($C_6H_6O_3$, which, according to Peratoner and Tamburello, has the constitution $\left.\begin{array}{l} CH\cdot O\cdot C\cdot CH_3 \\ \|\qquad\quad\ \| \\ CH\cdot CO\cdot C\cdot OH \end{array}\right)$, and γ-valerolactone were separated. With lapse of time or under the action of bacteria, etc., cellulose undergoes various changes (*see* Peat, Lignite, Coal, Vol. I., pp. 443 *et seq.*; and Methane, p. 33 of this Vol.).

With hot 1 per cent. sulphuric acid, pure cellulose yields only traces of formic and acetic acids, of which wood, straw, etc., yield as much as 2·8 per cent., the formyl and acetyl groups hence originating in the lignin. The acetic acid formed during the dry distillation of wood has a different origin from that obtained by heating with very dilute sulphuric acid.

Pure cellulose, which contains 0·04 per cent. of ash, has the absolute sp. gr. 1·58, and dissolves to the extent of 0·5 to 0·9 per cent. in 16 per cent. sodium hydroxide solution and, after boiling for 6 hours, to the extent of 2 per cent. in 3 per cent. sodium hydroxide solution. When dry it is an excellent electrical insulator, but its insulating power diminishes rapidly as its moisture content increases in the air. Suspended threads of cotton pass to the anode when a current passes. The hygroscopic moisture varies, with the degree of comminution of the fibre, from 5 to 8 per cent.

Pure cellulose remains unaltered up to 150°, but at higher temperatures begins to turn brown and decompose; if contaminated, even with oxycellulose, it decomposes at a lower temperature. When distilled it gives no methyl alcohol; the exothermal process during the distillation occurs at about 290° and is characterised by abundant separation of water.

Mineral acids, even when very dilute, hydrolyse cellulose more or less, and if any traces of acid remain during the drying of the product hydrolysis proceeds rapidly, causing diminished strength of the fibre and increased reducing power. Concentrated (or even 63 per cent.) sulphuric acid transforms cellulose into a colloidal solution; 69 per cent. acid gives *amyloid* and 78 per cent. acid *parchment*.

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triacetyl-compound is used for making artificial silk (*see later*), and is prepared by treating hydrocellulose in the cold with acetic anhydride, a few drops of concentrated sulphuric acid, and a little glacial acetic acid or phenolsulphonic acid.

More or less successful attempts have also been made to acetylate cellulose in the hot with acetyl chloride and metallic acetates, the reaction being facilitated by the addition of a small quantity of pyridine or quinoline and, in some cases, of a solvent of cellulose acetate (*e.g.*, acetone, nitrobenzene, naphthalene, etc.).

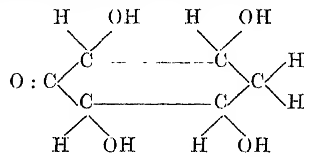
The following method of manufacture (from Fr. Pat. 347,906) admits of the direct acetylation of cotton textiles and may be taken as an example: 10 kilos of defatted cotton, containing 10 to 20 per cent. of moisture, are heated with 40 kilos of acetic anhydride (containing 0·25 per cent. of concentrated sulphuric acid) and 150 kilos of benzene, at 70° to 75°, in a reflux apparatus until a small portion of the cotton dissolves completely in chloroform; the whole mass is then pressed and dried.

Cross, Bevan, and Briggs (1907) obtain cellulose acetates easily and cheaply, without preparing hydrocellulose; cellulose is treated directly with a mixture of 100 parts of glacial acetic acid, 30 of zinc chloride, and 100 of acetic anhydride, the whole being heated for 36 hours at 45°.

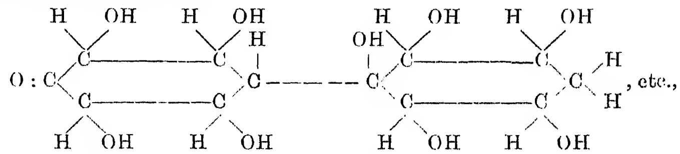
Cellulose acetate is largely used as "dope" for aeroplanes and as a coating for the fabric of airships to render them impermeable to gas. It forms a good electrical insulator.

The action of sulphuric acid on cellulose varies somewhat with the concentration of the acid, the duration of the reaction, and the temperature. The concentrated acid has a gelatinising action and dissolves part of the cellulose, which is reprecipitable by water or ammonia. If the action is protracted, the very friable **Hydrocellulose,** $C_{12}H_{22}O_{11}$ $[(C_6H_{10}O_5)_2, H_2O]$, is formed, but, in general, hydrocelluloses of diminishing molecular weight and increasing friability (*e.g.*, cellobiose; *see above*) are successively formed. The hydrocellulose formed in the preparation of artificial silk is only slightly friable, and has probably the formula $(C_6H_{10}O_5)_6$, H_2O. Since also these hydrocelluloses exhibit rather different behaviour towards dyes, it has been suggested that the name *hydrocellulose* be given to that resulting from advanced hydrolysis by non-oxidising acids; the increase of weight during this change, owing to the addition of hydrolytic water, is 3·5 to 5 per cent., this being lost at above 125°, whilst the hygroscopic moisture is expelled at 104°. This hydrocellulose reduces Fehling's solution (Ost; Cross and Bevan, 1909). On the other hand the name *cellulose hydrate* or *hydracellulose* is given to that obtained by gentle alkaline hydrolysis, which produces an augmentation in weight of 8 to 10 per cent.; here, too, this hydrolytic water is given up at temperatures above 125°. Hydrocellulose does not reduce Fehling's solution. Schwalbe (1907) measured the reducing power of hydrocellulose towards Fehling's solution.[1]

[1] Cross and Bevan proposed for cellulose the formula:



or some polymeride of this, such as



On the basis of the formation of the trinitrate and triacetate, Green (1894) suggested for *cellulose* a formula (or some multiple of it) containing 3 OH, namely:

CH(OH)—CH——CH(OH)\
| >O >O,\
CH(OH)—CH——CH₂—

and for *hydrocellulose* the formula

CH(OH)—CH——CH(OH)$_2$\
| >O ;\
CH(OH)—CH——CH$_2$·OH

these constitutions explain the formation of furfural by the decomposition of cellulose and also the formation, under the action of oxidising and bleaching agents, of *oxycellulose* containing ketonic groups which react with phenylhydrazine, reduce Fehling's solution, and admit of direct dyeing by basic dyes (*e.g.*, methylene blue). Two oxycelluloses are, however, distinguished: the one very similar to hydrocellulose and insoluble in boiling dilute alkali, and the other possessed of considerable reducing power and soluble in alkali.

The hardening of cellulose in the formation of wood is due to its partial transformation into **LIGNIN**, which is not yet well defined chemically but certainly contains methoxy-groups, which explain the formation of methyl alcohol and acetic acid when wood is distilled. According to Green, lignin is formed by dehydration of cellulose and would be a polymeride of

CH : C——CH·OH\
| >O >O\
CH : C——CH·OH

, but Klason is of the opinion that lignin is a kind of glucoside with two aromatic nuclei containing methoxy- and hydroxy-groups, also lateral groups, ·CH : CH and CH_2·OH, besides the fundamental cellulose grouping; it is probably represented by the formula $(C_{40}H_{42}O_{11})_n$, into which there enters a condensation product of coniferyl or isoconiferyl alcohol.

Dry wood contains 26 to 30 per cent. of lignin. Schultze, Tollens, and König hold the view that the hard part of wood is formed of cellulose, together with small proportions of pentosans and of lignin. The formation of wood in plants has been attributed by Wislicenus to the colloidal character of the plant fluids which, in the initial phase, transport into the tissues the cellulose-hydrogel as a superficial, chemically indifferent substance; in a second phase, the latter is lignified by absorption and surface gelatinisation of the colloidal metabolic substances contained in the sap. Lignocellulose is hydrolysed and dissolved by zinc chloride solution and by ammoniacal copper oxide solution, dilute acids and alkalis also exerting a hydrolysing action. Lignin gives a number of colour reactions, *e.g.*, with aniline sulphate (yellow), with phloroglucinol and hydrochloric acid (red); with potassium ferricyanide it forms potassium ferrocyanide, and with fuchsine decolorised by sulphur dioxide it gives a red colour; it fixes various aniline dyes

When sheets of pure, unsized paper are immersed for a few minutes in sulphuric acid of 50° to 60° Bé. and then washed immediately in a plentiful supply of water, they are converted into *parchment paper* (*artificial parchment*), amyloids being formed at the surface. These artificial parchments are distinguished from the natural ones by the presence of nitrogen in the latter, and from *paraffined paper* by the extraction of the paraffin from these by ether. Parchment paper is rendered softer and more transparent by immersion in glycerine or glucose solution. If cellulose pulp is well ground and beaten in the hollander until it forms an almost gelatinous pulp, a translucent paper can be obtained which is similar to artificial parchment and, under the name of *pergamin*, is largely used as a wrapping for foods and fatty materials ; this may easily be distinguished from vegetable parchment, which is composed of cellulose hydrate (amyloids) and is hence coloured blue by a solution of iodine in potassium iodide, whilst pergamin gives no such coloration.

With concentrated zinc chloride solution, cellulose gives compounds similar to those it forms with sulphuric acid : papers thus prepared and then superposed and compressed form the so-called *vulcan fibre* ; this is very hard, impermeable to water, and a bad conductor of electricity, and is used for making plaques, tubes, and noiseless gearing.

When cellulose is treated for a long time with energetic oxidising agents, it is converted into *oxycellulose* $(C_{18}H_{26}O_{16})_x$, which lowers the resistance of the tissues and, unlike cellulose, reduces Fehling's solution and fixes, although feebly, basic dyes and alizarine without a mordant. *Hydrocellulose* reduces Fehling's solution slightly and is not coloured by basic dyes.

When cellulose (spun or woven cotton) is treated in the cold with concentrated caustic soda solution (25° to 35° Bé.), it swells and becomes semi-transparent owing to the formation of *sodiocellulose*, and treatment of this with a large amount of water converts it into *hydrocellulose* (*see above*), the original appearance of the cellulose being retained. In the hot, however, sodiocellulose cannot be obtained (*see* Part III., Textile Fibres and Mercerised Cotton), prolongation of the action then resulting in decomposition into oxalic acid. Hygroscopic water held by cellulose is eliminated by heating at 100° to 105° ; the water of hydration in hydrocellulose is determined by heating in toluene or petroleum or at 130°. The hydration occurring during mercerisation increases the weight of the cotton by 8 to 10 per cent.

PAPER INDUSTRY

As prime material in the paper industry, use has been and is still made of all the cellulosic fibres obtained from most widely differing plants,[1] linen and cotton rags, straw, wood, hemp, etc.

(*e.g.*, methylene blue, eosin, etc.) directly. Wood is regarded by Cross and Bevan as an ester of lignocellulose, derived from cellulose (polyhydric alcohol) and *lignic acid* (lignin).

[1] **History of the Paper Industry.** The origin of paper dates back to the second century B.C., when the first traces of it were evident in China. In early times races marked their records and writings on stone, wood, and parchment. In the seventh and eighth centuries the Japanese and other neighbouring peoples learnt how to prepare paper from the bark of various trees, this industry then becoming known to the Arabs, but only much later in Europe. In 1190 paper made its appearance in Germany, in 1250 in France, in 1275 in Italy, and in 1430 in Switzerland.

In the East, besides bark, cotton and linen rags were also employed for paper-making. In Italy the first important factory furnished with grinders and pistons for the preparation of the raw material was erected at Fabriano in 1320. With the subsequent discovery of printing, the paper industry underwent an unforeseen and marked development, and grew to enormous proportions in the nineteenth century.

About the middle of the eighteenth century, the pistons and grindstones in use up to that time for treating the raw materials were gradually replaced by the so-called hollanders, which led to an increase in the output and an improvement in the quality of the product. The demand for paper increased largely at the end of the eighteenth century, the form being improved and the price lowered.

Mechanics and chemistry came to the aid of the paper manufacturer, and as early as the beginning of the nineteenth century the paste of cotton or linen fibres, mixed in large tanks, was transformed into a thin sheet of paper by means of a revolving, perforated drum, through which the water escaped. It was about 1825 that rudimentary *continuous machines* were first employed, these supplying an uninterrupted strip of paper a metre in width at a rate of 10 metres per minute. The imposing and complex, but very accurate, continuous machines of the present day give paper as much as 4 metres wide at 150 metres per minute.

Great advances were also made in the chemical treatment of the raw materials. In the first quarter of the nineteenth century, the putrefaction to which the rags were subjected so that

It is not possible here to review all the wonderful mechanical improvements which rendered paper-making one of the most interesting and important industries of the nineteenth century. From the arrival of the wood in the factory to the despatch of the rolls or reams of paper, all the operations are carried out mechanically by means of perfected machinery, which is not only more rapid in its action but more accurate than hand labour.

A description cannot be given here of all the varied and ingenious dressings employed to obtain different kinds of paper, or of the mineral *loading* of kaolin, barium sulphate, gypsum, etc., with which some papers are so impregnated that the mineral substances exceed the vegetable matter, to the delight of the tradesman who sells gypsum for cheese or sausages.

What will be attempted here will be simply a brief description of the various treatments to which the raw material is subjected to convert it into paper.

Paper factories require a plentiful supply of pure water, which must not contain iron and should be filtered if turbid.

The rags, gathered in places of all sorts and in all conditions, are acquired from the rag-merchants, who separate those of wool and silk, which go to wool factories, etc., and often sort the remaining linen and cotton rags into light and dark sorts.

The rags arrive at the paper factory in large bundles, some light and others dark. Preference is given to linen rags, since these give longer and tougher fibres and are used also to improve those of cotton. The first operation to which the rags should be subjected is disinfection, either by heat (great care being then taken to avoid fires) or by gaseous disinfectants (*e.g.*, by introducing the bales into large iron cylinders, which are then evacuated and filled with formaldehyde vapour). In many factories, however, this disinfection is omitted, the health of the sorters being thus jeopardised. *Sorting* is carried out by workpeople who spread the loose rags on tables and separate carefully those which are more

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they might be more easily disintegrated was replaced by heating with soda and lime in open boilers and, later on, in closed boilers under steam pressure. Then came bleaching of the fibres with gaseous chlorine and subsequently with chloride of lime. The yellow cellulose obtained from straw can also be bleached in this way, and since 1830 has been used in large quantities for the commoner papers and for mixing with rags. Sizing of paper by means of resin soap, although suggested in 1800, only later came into general use.

With the rapidly increasing consumption of paper, there came a time of dearth of raw materials; cotton and linen rags were no longer obtainable in sufficient quantities, and straw could not be used alone. It hence became necessary to look for other sources of cellulose, and it is to Keller that we owe the happy solution of this pressing problem. In 1843 he succeeded in utilising wood-cellulose by means of machines which, rotating rapidly against logs of wood kept wet, gradually converted the wood into an aqueous pulp made up of the separate fibres; these machines were improved later by Völter, and the first factories of *mechanical wood-pulp* were erected. This inexhaustible material can be purified by boiling it with caustic soda in digesters under pressure and bleaching the resultant brown mass with chloride of lime; this procedure gives *chemical wood-pulp*, which to-day forms the basis of almost all kinds of paper, from the finest to the commonest.

In 1884 Dahl effected considerable economy in the manufacture of wood pulp by replacing the expensive caustic soda to a large extent by sodium sulphate; calcination of the evaporated residue of the exhausted lye yields mainly caustic soda, sodium carbonate, sulphide, thiosulphate, etc., and a solution of this product acts on wood, giving a whiter and more resistant product. Although this process was applicable with advantage to straw cellulose, which gives good results only when treated with alkali or sulphate (the consumption of straw is limited nowadays by its increasingly high price), it was not convenient for dealing with the enormous quantities of wood necessary to meet the growing demands for paper. As early as 1865, Tilgman in America had attempted the chemical purification of mechanical wood-pulp by digestion with acid sulphites, and in 1874 Ekman's large factory at Bergvik was working regularly with magnesium bisulphite. Meanwhile, Professor Mitscherlich of Munich (1872) had suggested the improvement of this process by using calcium bisulphite in large digesters under pressure. From that time, and especially after the improvements introduced by Keller, the use of bisulphite spread gradually in Germany and other European countries and received a fresh impetus on the lapse of Mitscherlich's patents. At the present time, with rare exceptions—these including the treatment of straw, which contains silicates not attacked by bisulphite—almost all wood-pulp is transformed into cellulose by the bisulphite process. This process not only effects economy in the digestion of the wood-pulp, but results in an increased yield of a whiter and stronger product.

With improvements in the chemical methods and especially by the use of energetic bleaching processes (chlorine, chloride of lime, electrolytic alkali, hypochlorite, etc.), it became possible to utilise the wood of many different trees—from the fir to the poplar—so that there is now no danger that raw material for paper-making may some day fail. In Canada alone there are still forests large enough to supply the whole world with paper for 800 years, even with a much larger annual consumption than at present.

or less white and those which are coloured to varying degrees; the larger pieces are then cut by special cutters (Fig. 406), having a number of horizontal knives fixed to the periphery of a cylinder, the seams, buttons, hooks, etc., being previously removed. The different qualities then pass to suitable machines to be cleaned and brushed. Fig. 407 shows a simple form of *duster*, in which the rags are beaten vigorously by pegs on rapidly

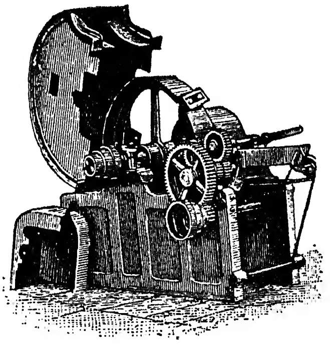

Fig. 406.

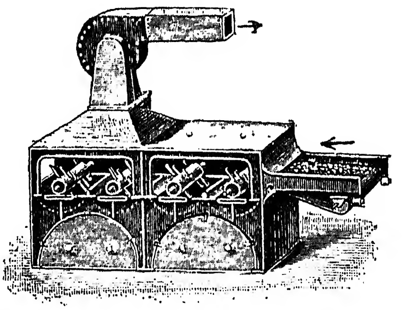

Fig. 407.

revolving horizontal wooden cylinders and carried to the opposite end of the machine, while the dust is removed by an air-draught to be deposited in chambers or in large bag-filters of various types (Fichter, Beeth, etc.).

After this the rags are washed a little with water in vessels similar to hollanders (*see* pp. 291 and 610) without knives but with a vaned wheel and a gauze drum for renewing the water. They are next removed to revolving spherical *boilers*, where the residual dirt is eliminated and any dye, fat, resin, starch, gum, or other impurity destroyed. This is effected by boiling, sometimes with soda or caustic soda, but more commonly with lime (2 to 5 per cent. on the weight of the rags) and water. These boilers (Fig. 408) hold as much as 2000 kilos of rags and make about two revolutions per minute, while steam is passed in through a tube traversing the axis until a pressure of 2 to 3 atmos. is reached. The boilers are coated with insulating material, and the boiling lasts for 6 to 12 hours, according to the nature of the material. When the boiling is finished, the steam under pressure is released into the adjacent boiler, in which the operation is just starting, and the rags removed, rinsed well in water, and reduced to a fine pulp in machines similar to hollanders (*see later*) with cast-iron or reinforced concrete tanks, the knives of the drum not being set too close to those of the fixed plate. About 20 horse-power is required by the hollanders for a charge of 200 kilos of rags. The loss in weight in all the operations up to the present stage varies, according to the quality of the material, from 12 per cent. to 40 per cent. In hollanders or similar vessels holding up to 800 kilos of rags, the bleaching is carried out with a clear solution of chloride of lime, of which 2 to 10 kilos are required per 100 kilos of rags; a little sulphuric acid (100 to 200 grms. per 10 kilos of chloride of lime) is finally added to liberate all the chlorine from the bleaching agent. In some factories fresh electrolytic solutions of sodium hypochlorite (*see* Vol. I., p. 572) are used. The bleaching must not be

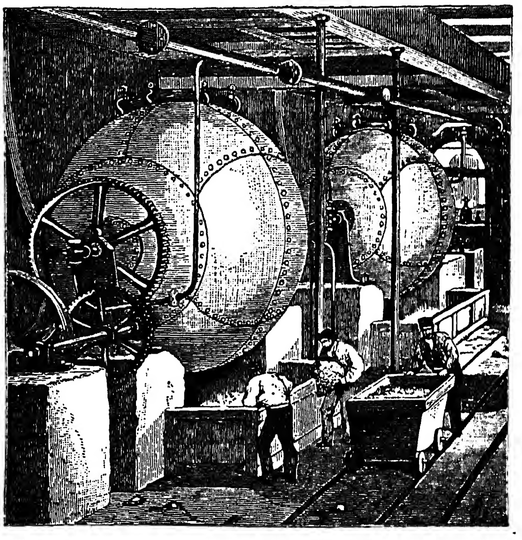

Fig. 408.

too prolonged, and the pulp is afterwards washed in large quantities of water until all smell of chlorine has disappeared and potassium iodide starch paper is no longer turned blue or blue litmus paper reddened; as a precaution, 30 to 50 grms. of sodium thiosulphate (antichlor) and soda are added to each vessel. The bleached mass or *half-stuff*, as it is called, is freed from water and allowed to drain for some days in brickwork chambers with floors of absorbent grooved bricks. From these it is taken in the moist state as required for mixing with bleached wood-pulp. The mixture is beaten in true hollanders, the knives being set more or less close according as more or less fine *refined pulp* is required.

WOOD-PULP (Mechanical Pulp). The treatment of the woody parts of the various plants suitable for paper-making [fir, pine, larch, poplar (*Populus nigra* or, better, *Populus canadensis*), beech, birch, esparto (of which Algeria exports half a million quintals annually), straw, hemp, broom, etc.] varies somewhat, as the cellulose and the surrounding lignin are present in different proportions and in different states of aggregation.[1] Logs containing few knots are cut into the required lengths (40 cm.), which, after the knots have been removed by a boring machine, are barked in another machine. The logs are then defibred by being pressed against a stone mill, which revolves rapidly and removes the fibres tangentially. This mill is about 1½ metre in diameter and 35 to 40 cm. thick, and it revolves either horizontally or vertically (at 150 to 180 turns per minute). To the latter type belongs the *vertical grinder* devised by Voith and subsequently improved in various ways (Figs. 409). The three chambers corresponding with the three toothed rods, *B*, contain the logs cut to the proper length, and, while the grinder revolves, these are pressed against it by the corresponding covers which are forced down by the toothed rods; the latter connect with gearing worked by a chain, *D*, the velocity of which is proportioned to that of the grinder. The pressure is nowadays

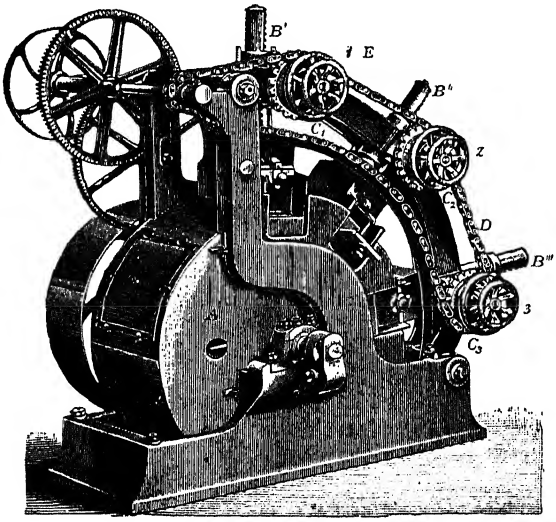

FIG. 409.

[1] In the disintegrated wood, the proportion of *cellulose* is determined by digesting several times with sodium bisulphite solution and then treating repeatedly with chlorine at 0°, by which means almost all the constituents except the cellulose are dissolved. For the determination of the *crude cellulose* in plants, Weender's older method, modified by Henneberg and Stohmann, has been largely replaced by that of Gabriel (or Lange and König): 2 grms. of the finely divided substance is heated in a beaker with 60 c.c. of alkaline glycerine (33 grms. of caustic soda dissolved in a litre of glycerine) at 180°, the mass being then cooled to 140° and poured into a basin containing 200 c.c. of boiling water, with which it is mixed and allowed to settle. The supernatant liquid is drawn off through a siphon covered with cloth at the end dipping into the liquid, and the deposit boiled with 200 c.c. of water which is siphoned off as before. The boiling is repeated with 200 c.c. of water containing 5 c.c. of concentrated hydrochloric acid, and the residue finally brought on to a tared filter, washed with water, alcohol, and ether successively, dried and weighed as crude cellulose.

To determine the *pure cellulose*, almost free from pentosans, ash, etc., König's method is used: 3 grms. of the finely divided, air-dried material is treated with 200 c.c. of glycerine (sp. gr. 1·230) containing 4 grms. of concentrated sulphuric acid in a dish which is heated in an oven at 137° for exactly one hour, the liquid being then allowed to cool to 80° to 100°, mixed with 200 to 250 c.c. of hot water, boiled and filtered hot through an asbestos filter with the help of a pump. The filter is then washed with 300 to 400 c.c. of hot water, then with boiling alcohol, and finally with a hot mixture of alcohol and ether. The filter with its contents is next introduced into a platinum crucible, which is dried at 105° to 110° and weighed. The crude cellulose is then ashed by heating to redness, the loss in weight thus produced representing the crude cellulose free from ash. If, in a second estimation, the cellulose is not dried and ashed, but is repeatedly treated for several hours with strong hydrogen peroxide and ammonia, and finally washed, dried, weighed, ashed, and again weighed, the proportion of pure, white cellulose is obtained. The difference between the crude and the pure cellulose represents the *lignin*.

exerted hydraulically; Fig. 410 shows a series of such vertical grinders in which hydraulic pressure is employed. Horizontal grinders (Fig. 411, vertical section; Fig. 412, general view) with hydraulic pressure are now widely used, as they admit of a larger number of logs being ground at the same time. While in operation, the grinder is continually sprayed with water to prevent heating and to remove the woody fibres as they are liberated.

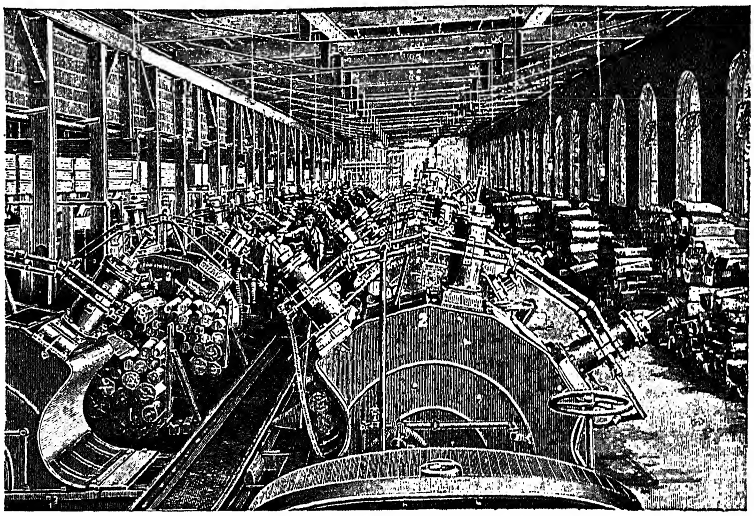

Fig. 410.

According to the pressure of the logs on the grinder and to the speed of the latter a more or less fine pulp is obtained with a smaller or larger content of splinters, dust, and other irregular and unusable portions; these are removed by means of sloping sieves, *B* and *C* (Fig. 413), on to which the channel, *A*, conveys the water to carry away the crude wood-pulp, while powerful water-jets carry the splinters (*b*), the good fibre (*c*), and the

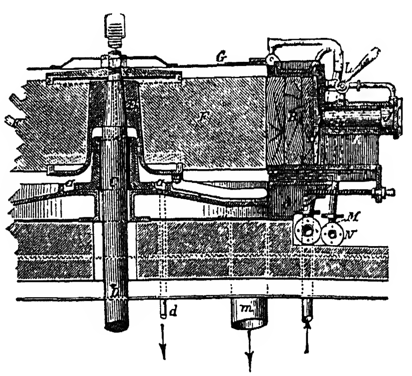

Fig. 411.

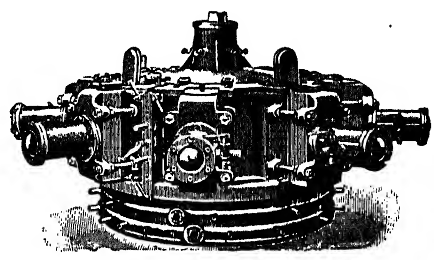

Fig. 412.

dust (*E*) to various collecting channels. Cylindrical or superposed sieves are also used. When the wood-pulp is to be used immediately for making paper, it is mixed with the necessary quantities of rag-pulp and dressing and worked up as described below, but generally the wood-pulp is placed on the market, in which case the water is removed and the pulp converted into sheets by sucking it on to drums of metal gauze or travelling planes, through which the water is drawn by suction; the continuous layer of pulp is cut into lengths and is best dispatched in the wet state (with 40 to 60 per cent. of water). Sometimes, however, the sheets are dried on hot drums, although this renders difficult the subsequent treatment necessary to transform them into pulp in the hollanders.

Wood-pulp is yellowish or rather brown, and still contains all the encrusting substance (lignin); it cannot be used as it is for paper, the action of light altering its colour immediately. It cannot be bleached with chloride of lime or alkaline reagents, which intensify its yellow colour, but good results are obtained with sulphur dioxide, which does not, indeed, remove the yellow tint but prevents the browning or reddening which gradually sets in.

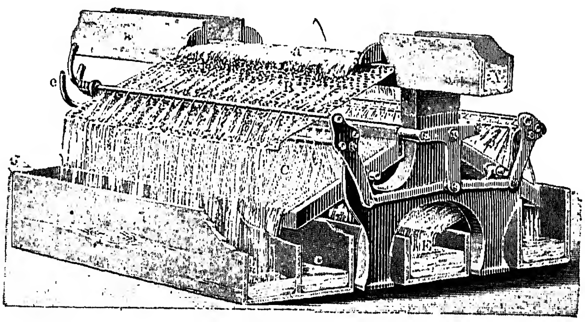

FIG. 413.

Barked and cleaned logs yield about one-half their weight of dry wood-pulp (containing 12 to 15 per cent. of moisture).

CHEMICAL WOOD-PULP. This is obtained by removing the encrusting matter from the wood or other raw materials (straw, hemp, *alfalfa*, *esparto*,[1] etc.) by means of various chemical agents. It was Payen who first, in 1840, attempted this purification with nitric acid, and who afterwards tried caustic alkalis, sulphurous acid, etc. The preparation of the cellulose in the chemical way can be effected by (*a*) the *soda process*, (*b*) the *bisulphite process*, (*c*) the *electric process*, (*d*) the *chlorine process*.

(*a*) The logs freed from bark and knots are converted into sticks 1 cm. thick, which are heated for some hours with caustic soda of 12° Bé. under a pressure of 6 to 8 atmos. (160° to 170°) in large digesters, 100 to 200 cu. metres in capacity. Various types of digester are in use, Fig. 414 showing the vertical type devised by Sinclair. This consists of an iron cylinder, A, 5 to 6 metres in height, with conical extremities, a charging orifice, C, a wide horizontal discharge tube, C_1, a tube, b, by which the caustic soda is introduced, and an inner perforated jacket, which is filled to the extent of four-fifths with the sticks. The reservoir, G, contains a supply of caustic soda solution, and circulation in the digester may be effected with the help of a Körting injector, the cocks of the tubes, h_1 and h, being opened; the latter conveys the alkali on to the sticks, while that collected between the perforated jacket and the inner wall of the digester ascends through h_1. The hot gases from the hearth, K, heat the digester and pass through E to the chimney. At the end of the operation the highly coloured alkali is discharged from the tap, V, and can be used for several successive treatments, being reinforced each time with a little sodium carbonate. The soda is eventually recovered from this liquor by evaporating in a vacuum, calcining the residue, extracting the sodium carbonate thus formed with water, boiling with milk of lime, and decanting the resultant caustic soda solution (*see* Vol. I., p. 554). But for this recovery of the soda, this process would be inapplicable. A method which is more economical and more generally used consists in reinforcing the alkali liquor first used with sodium sulphate, instead of the carbonate, for subsequent operations; the liquor is then ultimately evaporated in a vacuum and calcined, the sodium sulphate, in presence of carbonised organic matter, being converted partly into caustic soda and partly into sodium sulphide (which exerts

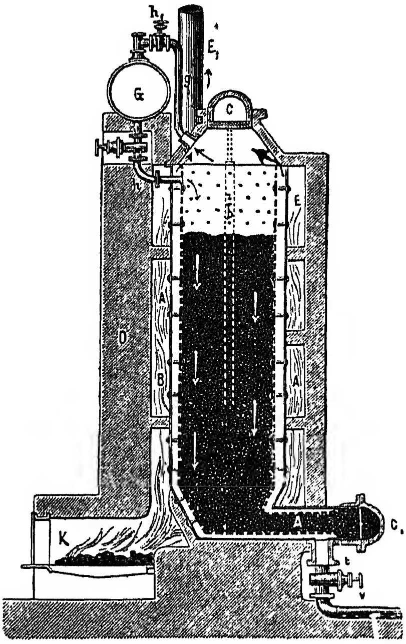

FIG. 414.

[1] *Esparto* and *alfalfa*, which are very similar, are the leaves of *Lygeum spartum* and *Stipa tenacissima* respectively, and are used for making nets, sandals, mats, ropes, paper, etc.

on wood the same action as caustic soda), just as in the preparation of soda by the Leblanc process (*see* Vol. I., p. 591). Extraction of the calcined mass with water yields a liquor containing sodium sulphate, sulphide, and carbonate, and is ready to act on fresh quantities of wood in the digester. Cellulose thus prepared is termed *sulphate pulp*. The concentration of the alkaline liquor is accompanied by the production of pungent and disagreeable odours, which are a source of annoyance to the neighbourhood, so that in certain countries (*e.g.*, Scandinavia) such concentration is prohibited. It has been suggested to destroy these odours (due to mercaptan) by nitrous vapours, or to condense the noxious fumes or pass them over metallic oxides.

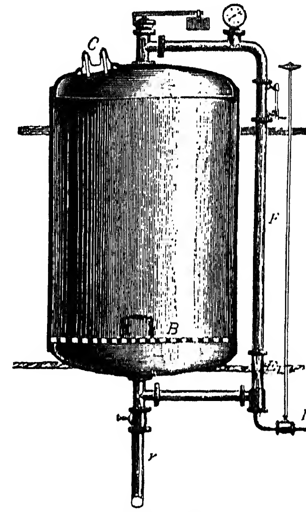

FIG. 415.

Use is also made of horizontal autoclaves arranged in series like sugar diffusors (*see* p. 549), while ordinary vertical iron digesters, as shown in Fig. 415, are largely employed. The digesters may be heated with indirect steam for 24 to 48 hours, or, more economically and rapidly, by direct steam (10 to 15 hours) to 140° to 150° (12 to 15 atmos.), but the yield is then rather lower and the mass slightly more attacked. The residual cellulose is washed, in the digesters themselves or in hollanders, with water and steam, and is then mixed with the quantity of rag half-stuff necessary for the kind of paper required, the whole being then worked in the hollander into the refined pulp (*see later*).

(*b*) *Calcium Bisulphite* (Mitscherlich) or *Magnesium Bisulphite* (Ekman) *Process.* This process is the one most largely used at the present time, as it gives a cellulose of better quality than the preceding method. The wood is heated under pressure (115° to 130° or 2·5 to 4 atmos.) in large autoclaves lined inside with cement or brickwork with a solution of calcium bisulphite, $Ca(SO_3H)_2$, or magnesium bisulphite, which dissolves the encrusting matter but does not act on the cellulose [1]; the liquid is circulated inside the boiler by means of an injector or by leaving a small upper tap slightly open. The bisulphite solution of 4° to 5° Bé. (about 30 grms. of SO_2 per litre, approximately one-third being combined with lime) is prepared in very tall wooden towers (that of Harpf being as much as 35 metres high), usually lined with lead and filled with limestone or dolomite (Fig. 416). A current of sulphur dioxide ascends from the bottom to the top of the tower, while the trough, b_1, supplied by the reservoir, S, at the top, yields a fine spray of water; the bisulphite solution is collected at the bottom. Harpf's tower has ten gratings (I to X), connected by steps not shown in the figure; each of these can be charged and attended to independently of the others by means of the door, k. The first six gratings are cleaned every four weeks, but the others far less often.

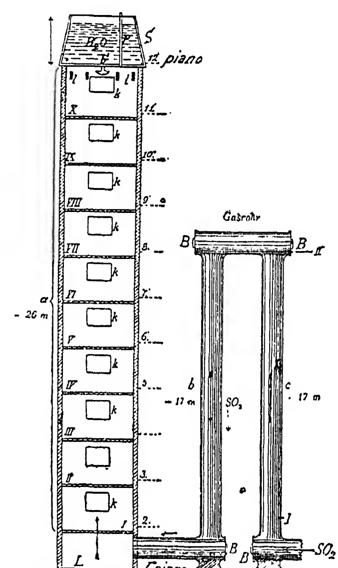

FIG. 416.

The sulphur dioxide issues from pyrites furnaces into the iron tube, c, and passes down the earthenware pipe b, B B being for convenience of cleaning. The calcium or magnesium bisulphite solution deposits its suspended matter in L and is then discharged into storage tanks. When

[1] *Lignin* is dissolved with remarkable ease by calcium bisulphite, giving a stable soluble compound, the sulphur dioxide in which is neither detectable by iodine, nor capable of being set free by sulphuric acid, nor able to exert reducing action. Sulphurous acid alone does not act so well as the bisulphite, the lime being necessary for the formation of these sulphonic salts and for the neutralisation of the sulphuric acid always formed.

the whole of the tower is to be washed, the plug, *P*, of the cistern is raised. Towers with bundles of wide vertical tubes are also used (Fig. 417).

Wood in logs is treated in suitable boilers, either horizontal as in the Mitscherlich process or vertical (Fig. 418) as in the Ritter-Kellner process. These are of iron and were formerly lined with thick lead to resist the action of the sulphurous acid, but now a lining of acid-resisting brick or special cement is preferred; the cocks are of phosphor-bronze.

To ascertain the completion of the action of the bisulphite on the wood in the digesters, a sample of the liquid is removed now and then and treated in a graduated tube with ammonia; when the calcium sulphite occupies one-sixteenth of the volume of the sample the heating is stopped, and when this fraction is reduced to one thirty-second the operation

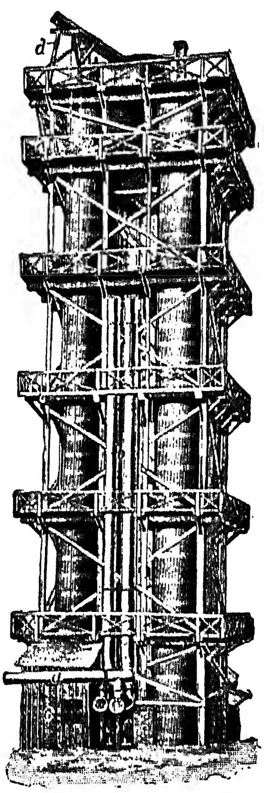

FIG. 417.

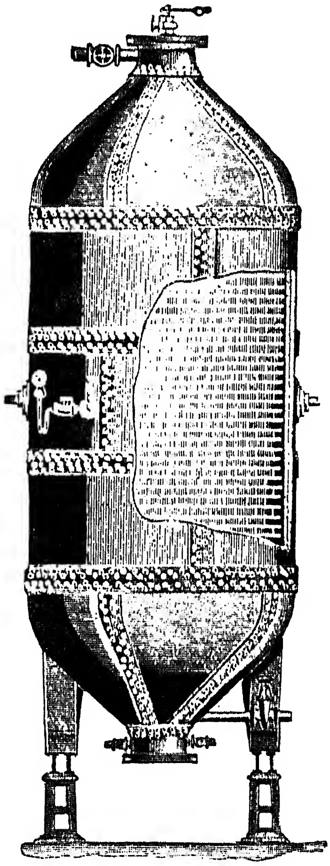

FIG. 418.

is finished and the coloured liquor can be discharged. The whole operation, including charging and discharging, preliminary treatment of the wood and action of the bisulphite, lasts 50 to 60 hours. The spent bisulphite liquor is highly coloured and charged with salts, gummy matters, tannin, glucose, pentoses, acetic acid, nitrogenous compounds, etc., and it is usually forbidden to turn it into watercourses or bottomless wells; so that it is often purified by precipitation of the sulphite with lime, the calcium sulphite being then reconverted into the bisulphite by sulphur dioxide. Attempts have also been made, but with little success, to evaporate the residual liquor and so obtain adhesive gummy substances utilisable in the preparation of coal briquettes. In a factory with two boilers, each of 120 cu. metres capacity (12 to 15 metres high, 3·5 to 4 metres in diameter, and about 2 cm. thick), each of these is charged with about 200 quintals of wood and 85 cu. metres of bisulphite solution. With a monthly output of 1000 quintals of cellulose, the daily production of spent liquor is 30 cu. metres, the organic residue amounting to 8 per cent. and the ash

to 2 per cent. The rational disposal of these spent liquors is always a serious problem, which still awaits solution; the attempts made to prepare alcohol from them are mentioned in the note on p. 169.

The yield of cellulose varies with the quality of the wood, but is about 40 to 55 per cent.

(*c*) *Electric Process.* This was proposed by Kellner, and consists in passing through closed receptacles containing the wood a solution of sodium chloride at 126°, through

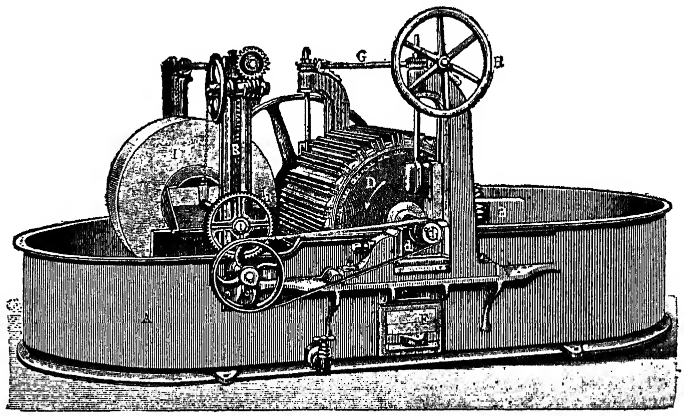

FIG. 419.

which an electric current passes; the chlorine, hypochlorous acid, and caustic soda act together in the nascent state, dissolving the encrusting substances of the wood and liberating the cellulose. This process has not yet been much used.

(*d*) *Chlorine Process.* This has been often attempted without success, but during recent years has been again tried on an industrial scale, owing to the large supplies of chlorine rendered available by the development of the electrolytic manufacture of caustic soda. The processes now being applied are derived from the analytical method proposed long ago by Cross and Bevan to separate cellulose from lignin.

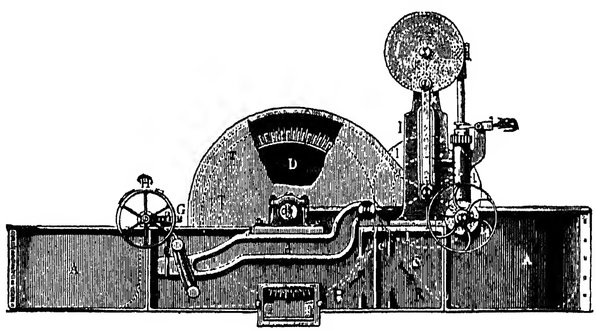

FIG. 420.

MECHANICAL REFINING OF THE CELLULOSE AND MECHANICAL WOOD-PULP. The mass of wood, more or less finely divided, extracted from the digesters is coarsely defibred in suitable disintegrating machines, and the cellulose and the mechanical pulp, either together or separately, according to the kind of paper required, are introduced into the so-called hollanders, where they are completely defibred and converted into a very fine pulp; bleaching with calcium hypochlorite and the subsequent washing are also carried out in the hollanders, as is the addition of dressing, colour, size, resin, alum, etc., necessary for the desired paper.

The hollander beating machine consists of a large, oblong wooden or, better, cement vessel (*A*, Figs. 419 and 420), in the middle of which is a vertical, longitudinal partition, *B*,

which does not extend to the ends of the vessel. In one part of the vessel is a large revolving drum, *D*, furnished at its periphery with a number of cutters which circulate the water containing the cellulose or mechanical pulp. The bottom of this part of the vessel is in the form of a ridge (*PR*, Fig. 420), and at a point, *F*, on one of the slopes are fitted cutters ; the drum can be moved up or down by means of the lever, *HG*, and the distance between its cutters and those at *F* thus adjusted as required. The movement of the water produced by the rotation of the drum causes almost the whole of the cellulose and pulp to pass between the fixed and revolving cutters, and after some time the woody fibres swim separately in the water. As the process goes on, the knives are gradually brought closer together until the desired degree of fineness is attained. The mass passes up the plane, *P*, down the plane, *R*, round the partition, *B*, again up the plane, *P*, and so on.

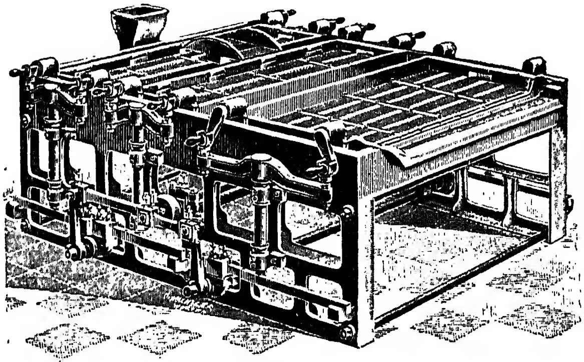

Fig. 421.

The washing water can be changed by immersing in the free half of the vessel a fine gauze drum from which the water can be aspirated by means of a pump. This drum is then raised by the chain and pulley, *R* (Fig. 419), and fresh water introduced into the vessel. To avoid spurting from the drum, *D*, it is fitted with a cover, *T*. In the base of the vessel and in front of the inclined plane is a recess for catching pieces of iron or stone accidentally present in the wood-pulp, the cutters thus being protected from damage. Fig. 206 on p. 291 shows a battery of hollanders, which are also used for guncotton.

SIZING AND FORMATION OF THE PAPER. The refined pulp in the hollander, containing the different raw materials (rags, wood-pulp, cellulose, etc.) in the requisite proportions, is blued and sized before being transferred to the continuous machines. The blueing is effected by adding, a short time before the end of the beating, 500 to 1000 grms. of ultramarine, Prussian blue, or aniline blue ; a little later the size is added, which renders the paper impervious to water and prevents ink from running on it ; if blotting-paper or filter-paper is required, the sizing is omitted. Sizing may be carried out on the finished paper, but it is usually preferred to add the dressing directly to the finished pulp while this is still suspended in water, since in this way all the fibres become coated with the size without losing the power of adhering, one to the other, to form a homogeneous, felted mass of paper. Animal size was at one time used, but, owing to its ready putrefaction or alteration even while it is being applied, it has been almost entirely replaced by resin (colophony) previously rendered soluble (resin soap) by means of caustic soda. With water this soap forms very fine, homogeneous and persistent emulsions, the efficacy of which may be increased by the addition of starch paste (in amount sometimes equal to that of the resin) or of casein dissolved in dilute soda solution. The total dressing added amounts to 2 to 5 per cent. of the dry paper.

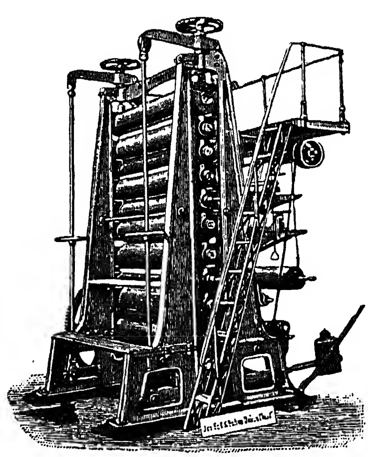

Fig. 422.

In order to precipitate the resin in a fine state of division on the fibres, a solution of aluminium sulphate (or of potash alum) is added to the homogeneous mixture of pulp and resin soap ; as was shown by Wurster, this effects the precipitation of the resin, starch (or casein), and a very small amount of aluminium resinate. Nowadays one-half of the aluminium sulphate is sometimes replaced by the cheaper magnesium sulphate. The

so-called *loaded papers* are obtained by adding, in addition, a considerable quantity (sometimes 50 per cent.) of kaolin, barium sulphate, talc, or calcium sulphate.

The colouring-matters (mineral dyes, lakes, or substantive aniline dyes) are also added directly to the finished pulp, organic dyes being the more commonly used. The lakes are produced by mixing basic dyes with the pulp and then precipitating with tannin solutions; for direct dyeing, substantive dyes (*see later*, Colouring-Matters) are employed. Powdered lakes obtained by precipitating either acid aniline dyes with aluminium hydroxide or basic dyes with tannin or tartar emetic may also be used.

After all these additions have been made, separation of any of the components from the homogeneous pulp is prevented by conveying the latter into two vats, where it is kept in motion by stirrers, the resultant milk being more or less dense according to the thickness of paper required. Before going to the continuous machine to be converted into paper, the pulp is passed through a purifier (Fig. 421) which removes any clots of fibre still present. This purifier consists of two or three slightly inclined, oscillating plates, perforated with very fine slots; when the pulp is fed regularly on to these plates, the fine fibres pass through while the lumps are discharged into channels provided for the purpose.

The homogeneous pulp collected under the vibrating plates is conveyed to the continuous machine at an almost absolutely regular speed, and on this depends the uniformity in the thickness of the resultant paper; the pulp regulator or feeder should hence be constructed with great care. If this homogeneous pulp is placed on a very fine sieve, the water passes through, leaving a thin layer of interlaced, adhering fibres which can be removed in

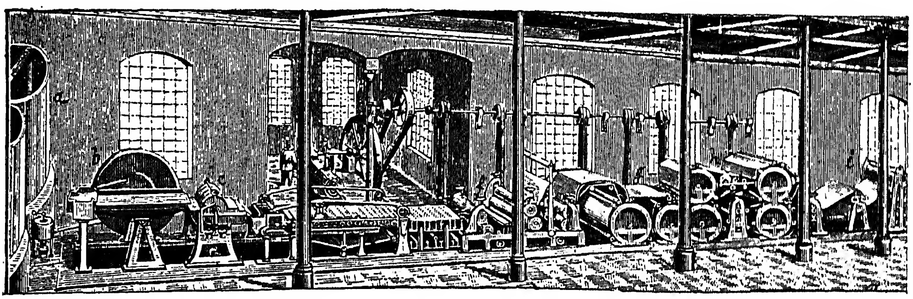

FIG. 423.

the form of a wet sheet. The preparation of the paper in the continuous machine takes place in a similar manner. The pulp is distributed uniformly on a very fine endless copper gauze after a good proportion of its water has been removed by draining and suction. A cloth then passes the wet sheet to a pair of rolls, which compress it and give it more consistency; other rolls heated to 130° gradually dry the paper, while others, again, press it and give it a little polish. When it leaves the endless gauze, the paper is sufficiently consistent to be conveyed to the supercalendar (Fig. 422), where it is pressed and polished between several pairs of rolls. Other machines wind it into rolls, cut it, rule it, etc.

A large modern continuous machine may cost several thousands of pounds. A general view of such a machine is shown in Fig. 423; the two vats of pulp are seen at *a*, while *b* represents the circular feeder carrying buckets, *c* the drum sieve which collects the pulp and passes it as a wet sheet to the metal gauze, *d*, this transferring it to the cloth at *f* and passing back round the rollers, *e*, underneath to take up fresh pulp; *g* shows the drying rolls and *h* where the cloth returns, the continuous length of paper being drawn off at *i* to the winding apparatus.

It is not possible here to consider the different kinds of paper now manufactured, or the different pulps required, or the special modern machines devised to meet all the requirements of the trade, but a few words may be devoted to the testing of paper,[1] the pulp

[1] **Testing of Paper.** The presence of *mineral loading* is detected by determining, in a platinum crucible, the *ash* of 1 to 2 grms. of the paper, cut up and dried at 100° to 105°; non-loaded paper contains 0·4 to 2·5 per cent. of ash. To detect the presence of mechanical wood-pulp, the paper is immersed in an aqueous solution of aniline sulphate, which imparts a golden-yellow colour to the crude wood fibre; or use may be made of aqueous phloroglucinol faintly acidified with hydrochloric acid, this dyeing the crude wood fibre (mechanical pulp) red. The *impermeability* or *solidity of the sizing* is determined by Leonardi's method; on to the paper,

used being recognisable under the microscope by the magnitude and form of the fibres (*see* Figs. 424 *et seq.*). As will be shown in the chapter on Textile Fibres, the fibres of paper are corroded and somewhat distorted and resemble the original fibres only in certain characters.

The fibres of the white fir are shown in Fig. 424 at *A* and in transverse section at *B*; they are brown and are characterised by the pores arranged in concentric circles. Fig. 425 shows at *B* altered cotton fibres and at *L* those of linen. Fig. 426 gives an idea of the microscopical appearance of mechanical wood-pulp of the conifers (fir, pine, etc.) with medullary rays, while Fig. 427 shows chemical pulp from the conifers; in the latter case, the concentric circular pores are less marked and the fibres more homogeneous. Fig. 428 shows straw cellulose with the very thin parenchymatous cells, *a*, rounded at the ends, and the superficial toothed cells of the epidermis, *o*, mixed with the bulk of ordinary elongated and striated fibres. *Esparto* fibres resemble those of straw to some extent but are lacking in thin and terminal cells, while the toothed edges are different in nature and are found in smaller cells than in straw; esparto contains certain isolated fibres having the form of teeth or elongated pears. Spain exported more than 90,000 tons of esparto in 1872 and about 46,000 in 1900. Algeria now exports 80,000 tons, Tunis 30,000, Tripoli 75,000 and Morocco 4000. Algeria contains 5,000,000 hectares under esparto. England imports about 200,000 tons of esparto per annum.

STATISTICS. Books and reviews often contain contradictory and fantastic statistics concerning the output of paper. According to the most trustworthy data, the world's production of paper and pasteboard in 1906 amounted to about 8,000,000 tons, and that of *cellulose* in 1908 was estimated at 1,600,000 tons of the value of £16,000,000, and in 1913 at 3,000,000 tons. In 1913 the paper industry of the world consumed 38,000,000 tons of

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stretched and inclined at 60°, a solution containing 1 per cent. of ferric chloride, 1 per cent. of gum arabic, and 0·2 per cent. of phenol is allowed to fall drop by drop so as to form a number of moist strips which are then allowed to dry; similar strips, crossing the first and perpendicular to them, are next made with a solution containing 1 per cent. of tannin and 0·2 per cent. of phenol; the formation of a black stain of tannate of iron at the point of intersection indicates bad sizing. absence of stain shows perfect sizing, and stains more or less grey denote more or less good sizing

Resin sizing is recognised by pouring a few drops of ether on to the paper and allowing them to evaporate; the formation of transparent rings indicates the probable presence of resin. Or a few grms. of the paper may be boiled with absolute alcohol containing a few drops of pure acetic acid, the solution being afterwards poured into distilled water; if the latter becomes turbid, the presence of resin is certain.

To detect *animal sizing*, a few grms. of the paper are boiled with a very small quantity of distilled water, the liquid being filtered, highly concentrated and treated with a solution of tannin; if size is present, whitish grey flocks are formed, which, when observed under the microscope in contact with a dilute solution of iodine in potassium iodide, are seen to be coloured brown, while if starch is present this is coloured blue; the test for starch may be made directly on the paper itself.

The presence of *free mineral acid* is ascertained by boiling the paper in a little distilled water and noting if the solution turns Congo-red paper blue or black.

For the *microscopical examination* (*see* Figs. 424–428), the fibres are liberated as follows: 3 to 5 sq. cm. of the paper is boiled and vigorously shaken for two minutes with 3 to 4 per cent. caustic soda solution, the pulp thus formed being poured on to a very fine metal sieve and washed well with tepid water. The fibres are then tested microchemically with solutions containing (1) 6 parts of iodine, potassium iodide, 10 parts of glycerol, and 90 of water, and (2) 100 parts of zinc chloride, 10·5 of potassium iodide, 0·5 of iodine, and 75 of water, the clear liquid being, in this case, decanted from the precipitate formed; linen, hemp, and cotton are coloured pale to dark brown by solution (1), the thin fibres remaining almost colourless, while with solution (2) a more or less intense wine-red coloration is obtained.

An alcoholic solution of phloroglucinol containing hydrochloric acid does not colour pure cellulose but reddens impure cellulose, the presence of wood-pulp (*i.e.*, impure cellulose) in paper being hence detectable in this manner. Further, aniline sulphate or naphthylamine hydrochloride colours impure cellulose yellow, but does not alter pure cellulose.

The *bursting strain* of paper, called also the *degree of elasticity*, is determined in the directions of the length and breadth by means of suitable dynamometric apparatus, the elongation which occurs before rupture being expressed as a percentage of the length (this varies from 1·5 to 4 per cent. for different papers). The *breaking length* expresses the length of a uniform strip of paper which would tear under its own weight if suspended from one end: if a strip 10 cm. wide of paper of which 1 sq. metre weighs 70 grms. breaks under a load of 3500 grms. the breaking ength is $\frac{3500}{70 \times 10} \times 1000 = 5000$.

The *resistance to folding* is determined roughly by crushing and rubbing an irregular ball of the paper between the hands; when different papers are compared in this way, that with the least number of creases is the best.

wood, valued at about £32,000,000, the consumption increasing by about 5 per cent. each year. In some countries as much as two-thirds of the wood used is converted into cellulose, 90 per cent. of the latter being obtained by the bisulphite process.

The following numbers represent the mean annual consumption of paper in kilos per inhabitant for various countries, these being regarded as a rough indication of progress :[1]

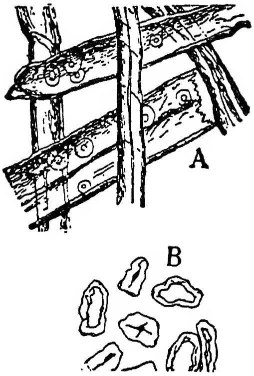


FIG. 424.

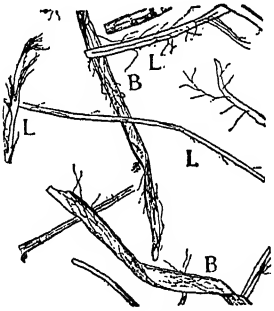


FIG. 425.

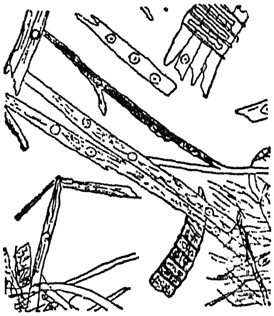


FIG. 426.

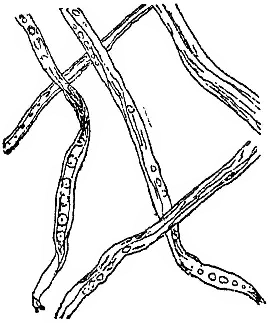


FIG. 427.

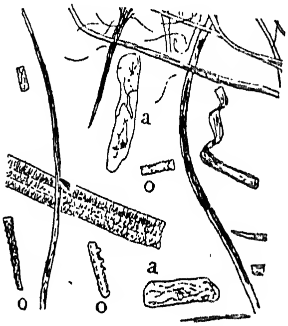


FIG. 428.

United States, 19·3 ; England, 17·2 ; Germany, 14 ; France, 11·5 ; Austria, 9·5 ; Italy 7·5 ; Spain, 2·5 ; Russia, 2·3 ; Serbia, 0·6 ; China, 0·6 ; India, 0·13.

[1] Prior to the War about 75,000 new books were published per annum throughout the world, these requiring 30,000 tons of mechanical pulp. In addition, some 70,000 daily papers are published with a total circulation of 11,000,000,000, these requiring 15,000 tons of mechanical pulp per day.

Of the total output of paper, 32 per cent. is for ordinary printing, 10 per cent. consists of fine paper and writing paper, 10 per cent. of brown paper and cardboard, 6·3 per cent. of fine cellulose and rag paper for fine printing ; 5 per cent. of straw paper and card, 3 per cent. of paper for placards, etc., 3 per cent. of wall-paper, 0·6 per cent. of drawing paper, 0·5 per cent. of silk paper, cigarette paper, and paper for making flowers ; 0·4 per cent. of blotting- and filter-paper, etc.

Although the consumption of paper has increased to an extent that would have been incredible a few years ago, yet the day is far distant when a scarcity of raw material will be experienced. Canada alone, with its 322,000,000 hectares of *forest land*, can supply the whole world for several centuries. Of other reserves of forest the most important are those of the United States, 200,000,000 hectares ; Russia, 184,000,000 ; Queensland, 86,000,000 ; Siberia, 38,000,000 ; British India and Burmah, 26,000,000 ; Finland, Sweden, and Japan (excluding Formosa and Hokkaido), 20,000,000 each ; Germany, 17,000,000 ; Austria and France, 10,000,000 each ; Hungary, Croatia, and Slavonia, 9,000,000 ; New Zealand, 8,000,000 ; Asiatic Turkey, 7,000,000 ; Norway, 6,000,000 ; Hokkaido (Japan), 6,000,000 ; Italy, 4,500,000, etc. In Burmah and elsewhere there are immense tracts of bamboo, which will one day be utilised for the manufacture of paper.

It cannot, however, be denied that an immense amount of wood is used for building purposes, and in Italy, for instance, many of the forests have been destroyed, so that the imports of wood, which in that country amounted to £840,000 in 1871, increased to £2,000,000 in 1900, to £2,840,000 in 1905, and to still greater extents (mostly from Austria-Hungary and America) in recent years (*see* Vol. I., p. 223).

CORK

This forms the principal component of the bark of the cork oak (*Quercus suber*), cultivated in Spain, Portugal, France, Italy, Algeria, Tunisia and Morocco. The corky bark may attain the thickness 25 to 45 cm., but in order to prevent it from deteriorating and cracking owing to excessive age, its collection is commenced after the tree is 15 to 20 years old. From each tree about 6 kilos of cork may be obtained every 10 years. The best qualities are golden-yellow, the poorer ones greenish-yellow.

The density of cork varies between 0·215 and 0·24, and increases with age. It consists of *suberin*, which is soluble in alcoholic potassium hydroxide, and of other substances yielding phellonic and other acids when hydrolysed with alcoholic potash. The percentage composition of air-dry cork is: water, 8; crude cellulose, 22 to 23; fats and resins, 4·6; various non-nitrogenous substances, 58; nitrogenous materials, 6; ash, 1·3.

From 8 to 12 kilos of cork 1 kilo of *cork stoppers* is obtained, the waste being utilised, either by agglomerating with pitch or chalk to make insulating material for the refrigerating industry, or for making *linoleum* (*see* p. 496), or for packing fruit, etc.

PART III. CYCLIC COMPOUNDS

THE aliphatic series contains various groups of closed-chain compounds (*e.g.*, lactones, uric acid derivatives, anhydrides of dibasic acids), which are readily opened by simple reactions giving ordinary open-chain compounds of the fatty series.

Numerous substances are, however, known containing a closed-chain nucleus which is composed of 3, 4, 5, or more commonly 6, carbon atoms united in a special manner and is resistant to the most energetic reagents. These compounds form the important group of isocyclic compounds.

Other groups of cyclic substances are also known with nuclei composed, not of carbon atoms alone, but of several elements, *e.g.*, pyridine, C_5H_5N, in which the nucleus contains 5 carbon atoms and 1 nitrogen atom; pyrrole, C_4H_5N, with C_4 and N in the nucleus; furan, C_4H_4O, with a C_4O nucleus; thiophen, C_4H_4S, with a C_4S nucleus; pyrazole, $C_3H_4N_2$, with the nucleus C_3N_2, etc. These compounds are called *heterocyclic*.

There are also many substances derived from more complex nuclei formed by the condensation of two or more of the nuclei mentioned above, *e.g.*, naphthalene, $C_{10}H_8$, in which are condensed two benzene nuclei held together by 2 carbon atoms common to the two nuclei, and quinoline, with a nucleus analogous to that of naphthalene but composed of one benzene and one pyridine nucleus.

AA. ISOCYCLIC COMPOUNDS

These contain 1 or several homogeneous carbon atom rings, and can be subdivided, according to the type of linking, into (1) **Polymethylene Compounds**, which contain singly linked carbon atoms and are less resistant to chemical reagents than (2) **Benzene Derivatives**, where the carbon atoms are linked very differently (*see later*). Compounds of the first group approach those of the aliphatic group in their chemical properties and are hence intermediate to methane and benzene derivatives.

I. CYCLOPARAFFINS AND CYCLO-OLEFINES OR POLYMETHYLENE COMPOUNDS

TRIMETHYLENE (Cyclo*propane*), $CH_2\!\left\langle\begin{matrix}CH_2\\ |\\ CH_2\end{matrix}\right.$, is obtained by the action of sodium on $\alpha\gamma$-dibromopropane, $CH_2Br \cdot CH_2 \cdot CH_2Br$, the bromine being eliminated as NaBr and the chain closed. It is a gas which liquefies at a pressure of 5 to 6 atmos. and combines very slowly with bromine or hydriodic acid giving open-chain compounds, so that it is easily distinguished from propylene $CH_2 : CH \cdot CH_3$. Its heat of combustion is much greater than that of propylene, into which it is partially converted at 400°.

Its derivatives are obtained from ethylene bromide by means of the ethyl malonate synthesis (*see* p. 369).

Trimethylenedicarboxylic Acid, $\left.\begin{matrix}CH_2\\ |\\ CH_2\end{matrix}\right\rangle C \left\langle\begin{matrix}CO_2H\\ \\ CO_2H\end{matrix}\right.$, was obtained by Perkin by the interaction of ethylene bromide and ethyl sodiomalonate.

TETRAMETHYLENE (Cyclo*butane*) is not known in the free state, but derivatives of it are obtainable by syntheses similar to those used for trimethylene compounds.

PENTAMETHYLENE (Cyclo*pentane*), $\left.\begin{array}{l} CH_2 \cdot CH_2 \\ | \\ CH_2 \cdot CH_2 \end{array}\right> CH_2$, is a liquid boiling at 50°; its derivatives are prepared by the ethyl malonate synthesis.

According to Baeyer's tension hypothesis (*see* p. 107 and Fig. 252, p. 366), it is easy to understand why pentamethylene is the most stable of the preceding compounds, a ring of five carbon atoms being the only one which can be formed without tension of the linkings. Indeed, while trimethylene combines with Br or HI with rupture of the ring, pentamethylene does not unite with bromine and resists the action of nitric or sulphuric acid like a saturated hydrocarbon, the properties of *saturated open-* and *closed*-chain compounds hence differing but little.

KETOPENTAMETHYLENE (Cyclo*pentanone*), C_5H_8O, is obtained by the dry distillation of calcium adipate:

$$\left.\begin{array}{l} CH_2 \cdot CH_2 \cdot COO \\ | \\ CH_2 \cdot CH_2 \cdot COO \end{array}\right> Ca = CaCO_3 + \left.\begin{array}{l} CH_2 \cdot CH_2 \\ | \\ CH_2 \cdot CH_2 \end{array}\right> CO;$$

by reduction and subsequent treatment with HI it gives *pentamethylene*, whilst oxidising agents convert it into glutaric acid, these reactions proving its constitution. Ketohexamethylene is obtained similarly by distilling Calcium Pimelate, $C_7H_{10}O_4Ca$, and higher homologues by distilling the corresponding calcium salts of higher dibasic acids; Calcium Suberate, $C_8H_{12}O_4Ca$, for example, yields Ketoheptamethylene (*suberone*). The yield diminishes with increase of the number of carbon atoms.

CYCLOPENTADIENE, $\left.\begin{array}{l} CH : CH \\ | \\ CH : CH \end{array}\right> CH_2$, is a liquid boiling at 41°, and is found in the first distillate of crude benzene and also in illuminating gas; it combines with iodine and with hydrogen sulphide. The presence of two double linkings in the nucleus is deduced from the fixation of four atoms of halogen. The two hydrogen atoms of the CH_2 readily react, *e.g.*, with acetone, giving intensely red *hydrocarbons*:

$$\left.\begin{array}{l} CH : CH \\ | \\ CH : CH \end{array}\right> CH_2 + \left.\begin{array}{l} CH_3 \\ \\ CH_3 \end{array}\right> CO = H_2O + \left.\begin{array}{l} CH : CH \\ | \\ CH : CH \end{array}\right> C : C \left<\begin{array}{l} CH_3 \\ \\ CH_3 \end{array}\right.;$$

this compound is known as Dimethylfulvene, fulvene being an isomeride of benzene of the structure $\left.\begin{array}{l} CH : CH \\ | \\ CH : CH \end{array}\right> C : CH_2$.

HEXAMETHYLENE (Cyclo*hexane, naphthene, hexahydrobenzene*), C_6H_{12}, is a colourless liquid, b.-pt. 81°, m.-pt. + 6°, and is obtained similarly to pentamethylene and also by hydrogenating benzene in presence of nickel (according to Sabatier and Senderens; *see* p. 35), platinum, or palladium. It occurs in Russian and Galician petroleum.

Numerous less hydrogenated derivatives, and also some with ketonic groups, are known. *Cyclohexanone*, an oil with the smell of mint, boils at 155°, is found in wood oil, and is converted completely into adipic acid on oxidation. Some of its derivatives occur in the decomposition products of cocaine and atropine.

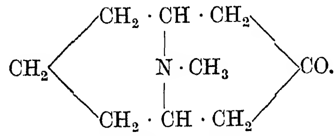
CYCLOHEPTANE (*Heptamethylene, suberane*), $(CH_2)_7$, is a colourless liquid, b.-pt. 117°, and is obtained by reducing suberone (*see below*); bromine and aluminium bromide contract the ring, *pentabromotoluene* being formed.

SUBERONE (*Ketoheptamethylene*), $(CH_2)_6 : CO$, is formed by the ketonic intramolecular transformation of the calcium salt of suberic acid. It is a liquid, b.-pt. 179°, and on oxidation gives pimelic acid and on reduction suberane (*see above*).

CYCLOHEPTATRIENE, $CH_2 \left<\begin{array}{l} CH : CH \cdot CH \\ \qquad\qquad\quad \| \\ CH : CH \cdot CH \end{array}\right.$, is a liquid, b.-pt. 116°, with the odour of leeks, and occurs among the products of the decomposition of cocaine and atropine. It

is obtained from suberone by complex reactions, and resembles olefines and not aromatic compounds ; thus it unites energetically with hydrobromic acid.

CYCLO-OCTANE, $(CH_2)_8$, is a liquid, b.-pt. 147°, and was obtained by decomposing an alkaloid, N-methylgranatonine, derived from the bark of the pomegranate tree and having the constitution



CYCLO-OCTATETRENE, C_8H_8, is a yellow liquid which behaves like the cyclo-olefines and not as an aromatic compound, although its constitution is analogous to that of benzene,

CH · CH : CH · CH
‖ ‖ With hydrogen in presence of spongy platinum it yields pure cyclo-
CH · CH : CH · CH.

octane. Such compounds are not in harmony with Baeyer's tension theory of valency.

II. BENZENE DERIVATIVES OR AROMATIC COMPOUNDS

It was observed by several chemists about the middle of last century that a whole series of compounds, mostly aromatic in nature, besides exhibiting certain common physical and chemical characters, showed on analysis proportions of hydrogen very low in comparison with those of carbon and also very low compared with those of hydrogen in saturated or unsaturated compounds of the methane series, *e.g.*, C_nH_{2n+2}, C_nH_{2n}, C_nH_{2n-2}, etc.

In general the hydrocarbons of these substances correspond with the fundamental formula, C_nH_{2n-6}, and the various transformations of the aromatic substances often yield Benzene, C_6H_6, from which they can again be prepared. If the constitutional formula of benzene were an open-chain one, it would be necessary to assume the presence of double or triple linkings between carbon and carbon which would lead to ready addition of bromine and to ready oxidation. These reactions do not, however, occur, and the great stability of the compounds of this group, and of benzene in particular, can be explained only by the existence of a stable nucleus of carbon atoms, probably joined in the form of a closed ring.

It was found later that benzene forms only one monosubstituted product (nitrobenzene, bromobenzene, etc.), and that all the hydrogen atoms of benzene exist under similar conditions ; three isomeric disubstituted products (*e.g.*, dinitro- or dibromo-benzene) are, however, known.

With the empirical formula C_6H_6 correspond the three rational formulæ : (α) $C_4(CH_3)_2$, (β) $C_3(CH_2)_3$, and (γ) $(CH)_6$. Formulæ (α) and (β) would give only two isomeric disubstituted products, whilst in the case of (γ), if the six CH groups were joined in the form not of an open-chain but of a closed ring, the six hydrogen atoms would be under the same conditions, and the formation of a single monosubstituted product and of three isomeric disubstituted products would be explained.

It was Kekulé who, in 1865, first advanced the ingenious hypothesis that the fundamental compound of aromatic substances is benzene, the constitutional formula of which must be represented as a closed, hexagonal chain of carbon atoms united alternately by single and double linkings, the fourth valency of each carbon atom being united to a hydrogen atom. Such an arrangement is figured in the scheme

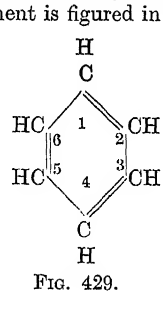


FIG. 429.

or, if the six carbon atoms are represented by tetrahedra, in the diagram shown in Fig. 430. The carbon atoms combined with the substituents in the three disubstituted derivatives would then be: (*a*) 1 and 2 (*ortho*-derivatives), (*b*) 1 and 3 (*meta*-derivatives), and (*c*) 1 and 4 (*para*-derivatives); the 1 : 5- and 1 : 6- compounds would be identical with the 1 : 3- and 1 : 2- compounds respectively. For the sake of shortness, the terms ortho-, meta-, and para- are contracted to o-, m- and p-, these being prefixed to the names of the compounds.

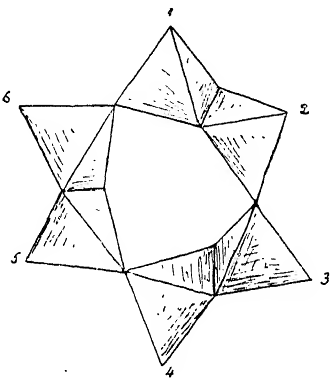


FIG. 430.

The constitutional formula given for benzene by Kekulé and also those of Claus (1867), Baeyer (1868), Körner (1869), and Ladenburg (1870) would seem to indicate the possible existence of 2 ortho-substituted derivatives, since the 1 and 2 carbon atoms are joined by a double linking and numbers 1 and 6 by a single linking. Hence Claus and Körner proposed the hexagonal formula with the fourth valencies of the carbon atoms joined diagonally (para-linking) (Fig. 431, *A*), while Ladenburg preferred the prismatic formula (Fig. 431, B_1, B_2, and B_3), and Armstrong and Baeyer the centric formula, with the fourth valencies in a latent (or potential) state and directed towards the centre (Fig. 431, *C*); *see also* Fig. 432.

In order to obtain a better interpretation of the formation of the disubstituted isomerides of benzene, Kekulé (1872) developed his theory further on the assumption that

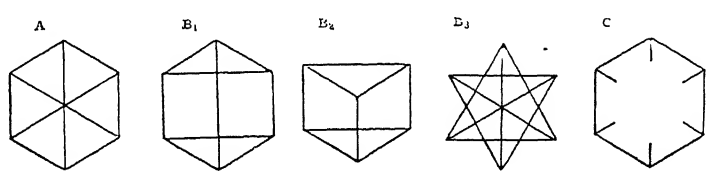


FIG. 431.

the linkings between the carbon atoms are to be regarded as vibrations, so that carbon atoms 2 and 6 of the Kekulé formula are in identical conditions. These oscillations would explain why benzene does not unite readily with halogens or ozone (*see* p. 107), or give Baeyer's permanganate reaction (*see* p. 107), thus behaving almost like a saturated compound. Even Kekulé's *oscillatory formula* does not, however, explain completely the optical and thermal behaviour of the aromatic compounds or the interesting results of Baeyer's work on the hydrogenated derivatives of benzene subsequently to 1886. Indeed, when two or four hydrogen atoms are added to benzene so as to form dihydro- or tetrahydrobenzene, the latter are found to be quite different from true aromatic compounds and to resemble olefine compounds; it must, then, be assumed that where the hydrogen has not been added, true double linkings are formed capable of combining with halogens or ozone and of giving Baeyer's permanganate reaction. Baeyer's centric formula would harmonise with this behaviour, since each of the valencies directed towards the centre is kept in equilibrium with all the others, stability being thus conferred on the molecule; if, then, two or four of the central valencies are used in the addition of hydrogen or other groups, the remaining central valencies becomes true, olefinic, double linkings.

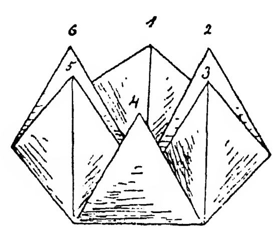
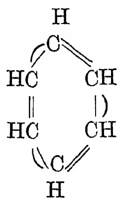


FIG. 432.

There are, however, aromatic compounds, especially those with several condensed benzene nuclei, with which Baeyer's centric formula alone cannot be assumed. In 1899 Thiele attempted to harmonise all the chemical and physical phenomena observed with benzene and its derivatives on the assumption that when two carbon atoms are united

by a double linking the two affinities are not completely utilised, parts of the unsatisfied valencies (*partial valencies*) remaining. These are regarded as bringing about addition processes, and are represented by dotted lines, *e.g.*, $\underset{\vdots}{C} = \underset{\vdots}{C}$, $\underset{\vdots}{C} = \underset{\vdots}{C} - \underset{\vdots}{C} = \underset{\vdots}{C}$, etc., but when, as in the latter formula, a conjugated system of double bonds is present, the addition of hydrogen, halogens, etc., occurs only at the two extreme carbon atoms, the partial valencies of the two middle atoms forming a new *inactive double bond*, $\underset{\vdots}{C} = C - C = \underset{\vdots}{C}$; after the addition at the extreme carbon atoms, the central inactive bond *becomes active again*, the constitution then being, $\underset{H}{\overset{}{C}} - C = C - \underset{H}{C}$. In Kekulé's benzene formula, we may assume the existence of three conjugated double bonds with three inactive bonds, thus,

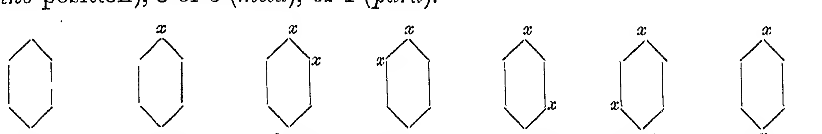


; it would then be clear why benzene, being without partial valencies, would not readily form additive products, and why, when even a single inactive double bond is broken down, true active olefinic double linkings would appear (*see* Theory of Double Linking, *Note* on p. 107).

A plausible explanation of the constitution of benzene is also arrived at by means of the ideas of *motochemistry*, according to which double or single linkings are represented by double or single vibrations or blows per unit of time (E. Molinari, *Gazzetta Chimica Italiana*, 1893, Vol. II., p. 47, and *Journal für praktische Chemie*, 1893, p. 113).

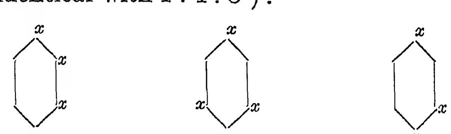
ISOMERISM IN BENZENE DERIVATIVES

It has been seen already that when one of the hydrogen atoms of benzene is replaced by a halogen or an organic residue, the same monosubstituted compound is always obtained, no matter at what point of the molecule the substitution occurs. If two substituent groups, either similar or different, are introduced, three disubstituted derivatives are obtainable. If the benzene molecule is represented simply by a hexagon, each angle of which indicates a carbon atom united with a hydrogen atom, replacement of the latter by another atom or group (x, y, z, etc.) may be shown by placing the symbol of the substituent at the angle of the hexagon. With disubstituted compounds, if one group is assumed to occupy the position 1, the other may go to either 2 or 6 (*ortho*-position), 3 or 5 (*meta*), or 4 (*para*).



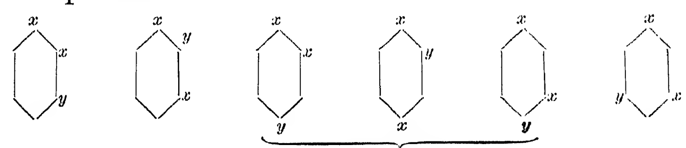
Benzene — Monosubstituted benzene — Ortho-compounds 1 : 2- and 1 : 6- (identical) — Meta-derivatives 1 : 3- and 1 : 5- (identical) — Para-derivative

With the trisubstituted derivatives, three isomerides are possible when the three substituents are similar (1 : 2 : 3- or *vicinal*, identical with 1 : 6 : 5- ; the symmetrical, 1 : 3 : 5-, identical with 2 : 4 : 6- ; and finally, the unsymmetrical, 1 : 2 : 4-, identical with 1 : 4 : 5-) :



Vicinal (*v*-) — Symmetrical (*s*-) — Unsymmetrical (*as*-)

When one of the three substituents is different from the remaining two, six isomerides are possible :



Vicinal Unsymmetrical Symmetrical

With four similar substituent groups, it will readily be seen that three isomerides are possible.

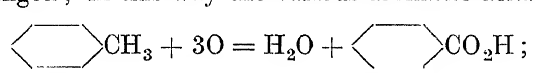
The number of isomerides may be further increased in cases where one or more of the substituents form lateral chains capable of isomerism, *e.g.*, saturated hydrocarbon or unsaturated alcohol or acid groups ; in these compounds, further replacement of hydrogen may occur either in the benzene nucleus or in the side-chain, fresh cases of isomerism being thus possible.

It was Körner (1869–1874) who first showed how it is possible to determine experimentally the *positions* of the various substituent groups in the benzene nucleus ; examples will be given later.

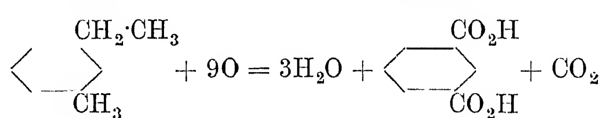
GENERAL CHARACTERS OF BENZENE DERIVATIVES

While the saturated hydrocarbons of the aliphatic series offer considerable resistance to oxidising agents and to concentrated sulphuric or nitric acid, those of the aromatic series readily give nitro-derivatives with nitric acid, and sulphonic derivatives, having an acid character, with sulphuric acid : $C_6H_6 + HNO_3 = H_2O + C_6H_5 \cdot NO_2$ (*nitrobenzene*) ; $C_6H_6 + H_2SO_4 = H_2O + C_6H_5 \cdot SO_3H$ (*benzenesulphonic acid*). In the latter, the sulphur is united directly to a carbon atom of the benzene nucleus, this being confirmed by the fact that benzenesulphonic acid is also obtained by the action of oxidising agents on thiophenol, $C_6H_5 \cdot SH$, in which the sulphur is known to be joined to carbon.

Oxidation of aromatic hydrocarbons containing side-chains leads to the replacement of the latter by *carboxyl* groups, CO_2H, the benzene nucleus remaining unchanged ; in this way the various aromatic acids are obtained :



Toluene Benzoic acid



Ethyltoluene Isophthalic acid

The halogen substitution derivatives, which are readily obtained by the direct action of the halogens, have less reactive properties than the halogen compounds of the aliphatic series and are more resistant to substitution.

The hydroxyl-derivatives (*e.g.*, phenol, $C_6H_5 \cdot OH$) are more decidedly acid in character than the alcohols of the fatty series, the *phenyl* group, C_6H_5, for example, being more negative than the ethyl group ; their resistance to oxidising agents is similar to that of the tertiary alcohols, to which they are analogous in constitution, the group $>C \cdot OH$ being present in both cases.

The amino-derivatives, which are readily obtainable by reducing the nitro-derivatives ($C_6H_5 \cdot NO_2 + 6H = 2H_2O + C_6H_5 \cdot NH_2$, aniline) with intermediate formation of azo-compounds (*q.v.*), are easily converted by the action of nitrous acid into diazo-compounds ; the latter are formed only seldom and with difficulty in the case of aliphatic compounds.

In their last investigations Körner and Contardi (1908) show how, with the

substitution products of benzene, the formation of one isomeride rather than another sometimes depends on minimal differences in the physical conditions under which the reactions take place. Thus, in the nitration of aniline or of halogenated derivatives, a very slight difference in the concentration (even in the second decimal place of the specific gravity) is sufficient to alter the yield very considerably or even to give entirely different products.

FORMATION OF BENZENE AND ITS DERIVATIVES

When vapours of aliphatic compounds are passed through red-hot tubes, the products formed contain aromatic compounds. At a red heat acetylene gives benzene (the reverse reaction is also possible): $3C_2H_2 = C_6H_6$.

Another source of aromatic products is the distillation of lignite tar or petroleum residues (*see* Cracking Process, p. 87).

When allylene, C_3H_4, is distilled with dilute sulphuric acid, mesitylene, $C_6H_3(CH_3)_3$ (1 : 3 : 5), is obtained, while under similar conditions crotonylene, C_4H_6, forms hexamethylbenzene, $C_6(CH_3)_6$.

In presence of concentrated sulphuric acid, several aliphatic ketones undergo condensation to aromatic hydrocarbons; thus, acetone forms 1 : 3 : 5-trimethylbenzene, $3C_3H_6O = 3H_2O + C_6H_3(CH_3)_3$.

Acetoacetaldehyde, $CH_3 \cdot CO \cdot CH_2 \cdot CHO$, when liberated from its sodium derivative, is transformed immediately into triacetylbenzene, $C_6H_3(COCH_3)_3$.

Various aromatic compounds may also be obtained by the action of sodium on ethyl bromoacetoacetate or ethyl succinate, by heating ethyl sodiomalonate and by certain other syntheses.

From the tar obtained by distilling coal, wood, or lignite, many aromatic compounds can be separated: 5 to 10 per cent. of naphthalene, 1 to 1·5 per cent. of benzene and toluene, besides quinoline, anthracene, etc.

Benzoic and salicylic acids, bitter almond oil, etc., occur naturally in the vegetable kingdom.

A. AROMATIC HYDROCARBONS.

Those with saturated side-chains are colourless, refractive liquids of characteristic odour, insoluble in water, but extremely soluble in ether or absolute alcohol; they are lighter than water (0·830 to 0·806).

General Methods of Preparation. (1) Alkyl chlorides and aromatic hydrocarbons in presence of aluminium chloride give mono- and poly-substituted hydrocarbons, which can be separated by fractional distillation: $C_6H_6 + CH_3Cl = HCl + C_6H_5 \cdot CH_3$ (Friedel and Craft's synthesis); intermediate aluminium compounds are first formed. Ferric chloride, zinc chloride, or zinc turnings act in the same way as aluminium chloride. The latter salt also brings about the decomposition of the higher hydrocarbons into more simple ones.

(2) In presence of sodium, monobromo-substitution derivatives of aromatic hydrocarbons and alkyl bromide or iodide give higher aromatic hydrocarbons (Fittig's synthesis, analogous to that of Wurtz for the aliphatic series):

$$C_6H_5Br + C_2H_5I + Na_2 = NaBr + NaI + C_6H_5 \cdot C_2H_5.$$

(3) Distillation of calcium salts with soda lime (analogous to the synthesis of aliphatic hydrocarbons):

$$\underset{\text{Calcium benzoate}}{(C_6H_5CO_2)_2Ca} + Ca(OH)_2 = 2CaCO_3 + 2C_6H_6.$$

(4) Aromatic sulphonic derivatives give the hydrocarbons when heated with sulphuric or hydrochloric acid, best in presence of steam: $C_6H_5 \cdot SO_3H + H_2O = H_2SO_4 + C_6H_6$. On this reaction is based the method used for separating aromatic hydrocarbons from those of the aliphatic series, the former with concentrated sulphuric acid giving soluble and the latter (paraffins) insoluble sulphonic acids.

(5) When an aromatic hydrocarbon is dissolved in an alcohol in presence of zinc chloride at about 300°, water separates and a higher hydrocarbon is formed: $C_6H_6 + C_5H_{11}OH = H_2O + C_6H_5 \cdot C_5H_{11}$.

COAL TAR

The cheapest and most abundant hydrocarbons used as raw material for the preparation of large numbers of important aromatic compounds (from artificial perfumes to aniline dyes) are obtained by the distillation of tar. While at one time this product constituted an unpleasant and inconvenient residue of the illuminating gas industry (*see* pp. 40 *et seq.*), it is now so much in demand by large manufacturers of chemical products that it is sometimes very scarce, and attention has been turned to the utilisation of the tar produced in metallurgical coke factories, this having been formerly discarded.[1]

Westphalian coal gives, on an average 2·5 per cent. of tar, that of Saar as much as 4 per cent., and that of Silesia even more than 4 per cent.

COMMONEST AROMATIC HYDROCARBONS WITH A SINGLE BENZENE NUCLEUS.

	Name	Rational formula	Position of substituents	Melting-point	Boiling-point	Specific gravity
C_6H_6	Benzene	—	—	+ 5·4°	+ 80·4°	0·874 $\left(\frac{20°}{4°}\right)$
C_7H_8	Toluene or methylbenzene	$C_6H_5 \cdot CH_3$	—	liquid	110°	0·869 (16°)
C_8H_{10}	*o*-Xylene = *o*-dimethylbenzene	$C_6H_4(CH_3)_2$	1 : 2	— 28°	142°	0·893 (0°)
	m-Xylene = *m*-dimethylbenzene	,,	1 : 3	— 53°	139°	0·881 (0°)
	p-Xylene = *p*-dimethylbenzene	,,	1 : 4	+ 13°	138°	0·880 (0°)
	Ethylbenzene	$C_6H_5 \cdot C_2H_5$	—	liquid	136°	0·883 (0°)
C_9H_{12}	Hemimellithene = trimethylbenzene (*v*)	$C_6H_3(CH_3)_3$	1 : 2 : 3	,,	175°	—
	Pseudocumene = trimethylbenzene (*as*)	,,	1 : 2 : 4	,,	169·5°	0·895 (0°)
	Mesitylene = trimethylbenzene (*s*)	,,	1 : 3 : 5	,,	165°	0·865 (14°)
	n-Propylbenzene	$C_6H_5 \cdot C_3H_7$	—	,,	159°	0·867 (14°)
	Isopropylbenzene = cumene	,,	—	,,	153°	0·866 (16°)
$C_{10}H_{14}$	Prehnitene = tetramethylbenzene	$C_6H_2(CH_3)_4$	1 : 2 : 3 : 4	— 4°	204°	—
	Isodurene = tetramethylbenzene (*as*)	,,	1 : 2 : 3 : 5	liquid	195°	—
	Durene = tetramethylbenzene (*as*)	,,	1 : 2 : 4 : 5	+ 80°	192°	—
	m-Cymene = methylisopropylbenzene	$C_6H_4 \cdot CH_3(C_3H_7)$	1 : 3	liquid	175°	0·862 (20°)
	Cymene = methylisopropylbenzene	,,	1 : 4	,,	175°	0·856 (20°)
	n-Butylbenzene	$C_6H_5 \cdot C_4H_9$	—	,,	180°	0·864 (15°)
	sec. Butylbenzene	,,	—	,,	175°	0·867 (15°)
	Isobutylbenzene	,,	—	,,	171°	0·871 (15°)
	tert. Butylbenzene	,,	—	,,	167°	0·871 (15°)
$C_{11}H_{16}$	Pentamethylbenzene	$C_6H(CH_3)_5$	1 : 2 : 3 : 4 : 5	+ 51·5°	231°	0·847 (104°)
	n-Amylbenzene	$C_6H_5 \cdot C_5H_{11}$	—	liquid	202°	0·860 (22°)
	Isoamylbenzene	,,	—	,,	194°	0·885 (18°)
$C_{12}H_{18}$	Hexamethylbenzene	$C_6(CH_3)_6$	1 : 2 : 3 : 4 : 5 : 6	+ 166°	265°	—
$C_{13}H_{20}$	*n*-Heptylbenzene	$C_6H_5 \cdot C_7H_{15}$	—	liquid	109° (10 mm.)	—
$C_{14}H_{22}$	*n*-Octylbenzene	$C_6H_5 \cdot C_8H_{17}$	—	— 7°	263°	0·852 (14°)
$C_{16}H_{26}$	Pentaethylbenzene	$C_6H(C_2H_5)_5$	1 : 2 : 3 : 4 : 5	liquid	277°	0·896 (20°)
$C_{18}H_{30}$	Hexaethylbenzene	$C_6(C_2H_5)_6$	1 : 2 : 3 : 4 : 5 : 6	+ 129°	298°	0·830 (130°)
$C_{22}H_{38}$	Cetylbenzene	$C_6H_5 \cdot C_{16}H_{33}$	—	+ 27°	230° (15 mm.)	0·857 (27°)
$C_{24}H_{42}$	Octadecylbenzene	$C_6H_5 \cdot C_{18}H_{37}$	—	+ 36°	249° (15 mm.)	—
	Hexapropylbenzene	$C_6(C_3H_7)_6$	1 : 2 : 3 : 4 : 5 : 6	+ 118°	—	—
$C_{25}H_{44}$	Trimethylcetylbenzene	$C_6H_2(CH_3)_3(C_{16}H_{33})$	1 : 3 : 5 : 2	+ 40°	258° (15 mm.)	0·845 (40°)

[1] The first attempt to utilise tar dates back to 1834, when, in a works at Manchester, it was distilled out of contact with air in primitive retorts, the liquid products being collected and the residual pitch employed for making black varnish. Bethell subsequently patented a process for obtaining from tar creosote oil for the impregnation and preservation of wood.

Still later the more volatile products of the distillation of tar were used both as an illuminant and as a cleaning liquid. Nitrobenzene was then prepared from it to replace essence of mirbane, but it became possible to develop an industry for the regular utilisation of tar only after the wonderful discovery by Perkin (1856), who prepared synthetically the first artificial coal tar dye, thus laying the foundation of one of the most important industries for which the nineteenth century is famous.

Numerous industries then arose for the more complete and more rational utilisation of tar — for employing to the best advantage the various products of its fractional distillation. Since

After separation from the ammoniacal liquors of gas manufacture (by centrifugation), tar forms a dense, somewhat viscous, blackish (since it contains 10 to 30 per cent. of suspended carbon particles) liquid of sp. gr. 1·1 to 1·3. It contains many varied acid, basic, and indifferent products; the first can be extracted by agitating with aqueous alkali solution, the second with acids, while the neutral compounds, consisting principally of aromatic hydrocarbons, form the residue. The composition of tar varies, however, with the nature of the coal, the type of furnace, and the temperature of distillation.

It seems that tar contains at least 300 different substances, of which 150 have been established either directly or indirectly and 90 have been isolated with certainty and studied, although only four have wide application in the pure state: benzene, phenol, toluene, and naphthalene.

Only to a small extent is tar used as it is: for varnishes, coal briquettes, bitumenised paper, *lampblack*,[1] treating roads to render them less dusty, etc., but for such purposes the residue from the distillation of tar can also be used.

A little tar is used in preparing the basic lining of Bessemer converters for the manufacture of steel.

OTHER TARS. These include (1) **Lignite tar**, which consists mainly of paraffinoid hydrocarbons, both saturated and unsaturated, but contains also phenol, cresol, various bases, sulphur compounds, benzene and its homologues, naphthalene, naphthenes, paraffin wax, etc. It is dense and yellowish-brown or black with a greenish fluorescence, its sp. gr. being 0·82 to 0·95 at 45° and its m.-pt. 25° to 35°. When distilled it yields various light and heavy oils, creosote oil and hard and soft paraffin waxes (*see* pp. 95 *et seq.*). (2) **Wood tar or Vegetable tar** (*see* pp. 128, 333, 335) has the sp. gr. 1·06 at 15° and is of less value than coal-tar; its most important constituents are those soluble in alkali, these consisting of methyl ethers of polyhydric phenols (pyrocatechol, pyrogallol and homologues, forming

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that time a continuous series of mechanical improvements in the plant and chemical ones in the processes have been introduced. Improvements in the coke furnaces to admit of the collection of the whole of the products of distillation and of the rational recovery of the heat have been dealt with in Vol. I. (p. 451).

[1] **Lampblack** is prepared by the incomplete combustion of tar, colophony, vegetable oils, the pitch or heavy oils from tar, etc. The liquid or fused substance of the receivers, *a*, is passed through pipes to the long pans, *A* (Fig. 433), in which it is heated while a carefully regulated minimal air-current is passed over the surface of the liquid so as to burn the vapours incompletely and separate the greater part of the carbon in a free and finely divided state. This is carried away by the air into the first arched chamber, *B*, where it is partly deposited, then into the second arched chamber, *c*, and finally into *D* (before the chimney, *O*), in which the final traces

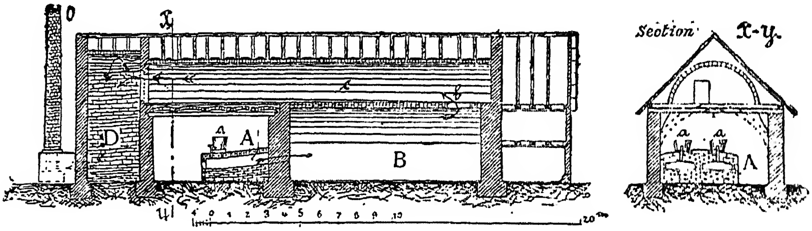


FIG. 433.

of lampblack are deposited on a thin cloth in front of the mouth of the shaft. This operation is continued for five days, the sixth day (Sunday) being occupied in cooling down and the seventh in restarting. A very fine lampblack is obtained by burning paraffin oil in a kind of lamp with a wide thin jet and allowing the flame to impinge on an iron cylinder inside which water circulates; the cylinder thus cools the flame and the lampblack deposited on it is removed from time to time by an automatic scraper. With more or less intense cooling the lampblack has a lower or higher specific gravity. 100 kilos of tar yield 25 kilos of lampblack, while 100 kilos of resin residue give 20 kilos. Lampblack contains, in addition to free carbon, tarry impurities and oily distillation products. Attempts have been made, apparently without success, to prepare lampblack by exploding acetylene with a measured proportion of air in closed vessels. The Frank process seems to be more advantageous; in this, acetylene is burned with a certain proportion of carbon monoxide or dioxide: $C_2H_2 + CO = H_2O + 3C$.

Before the War Swedish lampblack cost 16*s.* to 20*s.* per quintal, that from resinous wood 40*s.* to 52*s.*, and that from lamps £8 to £20. It is used for making black varnishes, printers' ink, boot polish, etc. *Boot polish* is made by mixing lampblack with wax, molasses, turpentine, and sometimes also sulphuric acid or a little chestnut tannin extract to preserve the skin or leather.

cresoste oil), which are used for making guaiacol. *Wood-tar* is distilled in a vacuum, the gases which do not condense being utilised for power or heating purposes, as they have a calorific value of 6000 to 9000 cals. per cubic metre. (3) Peat tar gives, when distilled, the following products (percentages): aqueous liquid, about 50; this contains 1·5 per cent. of acetic acid and about 2 per cent. of ammonia; coke, 33; gas, 8 to 10 (28 to 38 per cent. H_2, 20 to 25 CO, 6 to 10 CO_2, 32 to 38 CH_4, 8 to 12 of heavy hydrocarbons); tar, 8.

DISTILLATION OF TAR

Nowadays tar is mostly subjected to distillation for the extraction of the following products: (1) *Indifferent substances*, in which benzene hydrocarbons predominate (benzene, toluene, xylene, tri- and tetra-methylbenzene, and, to a still greater extent, naphthalene, anthracene, etc.), those of the methane series being small in amount (these occur abundantly in the distillation products of *lignite* or peat tar and of bituminous shale, *see* pp. 95-100). Small quantities of nitrogen compounds occur, such as acetonitrile, benzonitrile, carbazole, and pyrrole derivatives, and also traces of carbon disulphide, thiophene, cumarone, etc.; (2) *Acid substances*, among which phenol (carbolic acid), cresol, xylenol, and the naphthols abound. (3) *Basic substances*, which are found in small amount and contain small proportions of pyridine and quinoline compounds and a trace of aniline.

In order to prevent bumping and frothing over during distillation, tar must be completely freed from water, which it holds tenaciously. In gas works the wet tar passes continuously into a small tank *C* (Fig. 434) where the ammoniacal liquor overflows into *A*, while the tar is syphoned into *B*. Gypsum or cement is also used for removing the water.[1]

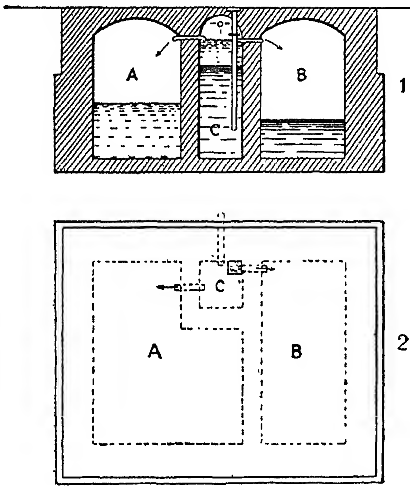


FIG. 434.

Treatment of the wet tar with water removes a large proportion of the ammoniacal liquor, this being especially advantageous when the tar is subjected to continuous distillation owing to the removal of ammonium compounds liable to obstruct the cooling coils and to prevention of corrosion by the hydrogen chloride produced by dissociation of the ammonium chloride. Application of heat first to the upper part of the boiler, and only later to the lower, is suggested for preventing aqueous tar from frothing over. The ammonia water may also be largely removed by centrifuging the tar. In large distilleries the dehydration and distillation of the tar are carried out simultaneously.

The old type of boiler is shown in Fig. 435, but preference is now given to horizontal stills, which are sometimes multitubular, like locomotive boilers, in order to obtain more homogeneous and more rapid heating.[2] It will be seen in the figure that direct-fire heat is used (at *b*); the mass is mixed at intervals by means of a stirrer or of a steam-jet introduced

[1] Estimation of water in tar is not easy, since when the tar is heated in a dish it readily froths and overflows. Beck and Rispler (1909 and 1904) allow 200 grms. of the tar to fall drop by drop from a separating funnel on to about 500 grms. of water-free heavy tar-oil contained in a flask of about 2 litres; each drop of tar, as it falls, is instantly evaporated, and the water distilling over is condensed in the refrigerator connected with the flask and collected, together with a little tar-oil, in a graduated cylinder; the temperature is finally raised to 300°. The cylinder is kept at a moderate temperature, so that the water separates from the oil; its volume is then read. If much naphthalene also distils over, it is difficult to read the volume of the water; in this case, the whole of the distillate is poured on to a small filter-paper steeped in benzene, so that only the tar-oil filters. The filter-paper is subsequently pierced and the water allowed to pass into a graduated cylinder. Ott, on the other hand, heats 400 grms. of tar in a copper retort, the heating being carried out from the top by means of an annular gas-pipe with orifices in its lower side.

[2] The rapid wear of the iron vessels and coils is due especially to HCl, NH_3, H_2S, HCN, etc., formed by the dissociation at high temperatures of chlorides (*e.g.*, ammonium chloride, dissociating at 360°), sulphides, cyanides, etc., and perhaps also by certain electrolytic processes. The base of the still is often 18 to 20 mm. in thickness. Cast-iron coils last better than those of wrought-iron, and are composed of superposed straight tubes connected at alternate ends by semicircular pipes of cast iron.

at x and subdivided on the arched base of the still by a number of pipes, z. The tar enters at r, and at the end of the operation the pitch is discharged through a much wider orifice than that marked a. A thermometer or pyrometer is inserted at v, while t serves as exit for the vapours, which are condensed in a coil surrounded by cold water in the case of the first products and by hot water in that of the last products; these are collected in order of density in a number of small receivers, from which they are passed to large store-tanks. The stills are arranged in batteries under light roofs open at the sides so that the damage in case of fire or explosion may be minimised, the further precaution being taken of placing the fire hearths outside in the open. When the products formed at 270° are distilled over, the yield is increased and the pitch rendered more liquid, and so prevented from charring, by introducing a current of superheated steam, this removing various substances (anthracene oil) which would otherwise remain in the pitch. The latter is then discharged, while hot, into old, disused steam boilers so as to avoid contact with the air, which might ignite the mass; when almost cold but still fluid, it is run into shallow vessels or pits dug in the earth and allowed to solidify.

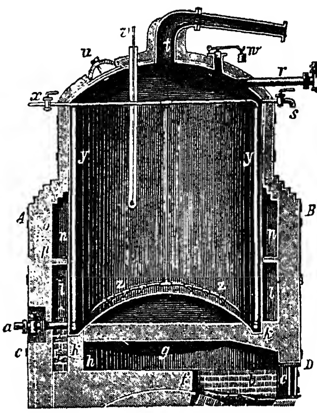
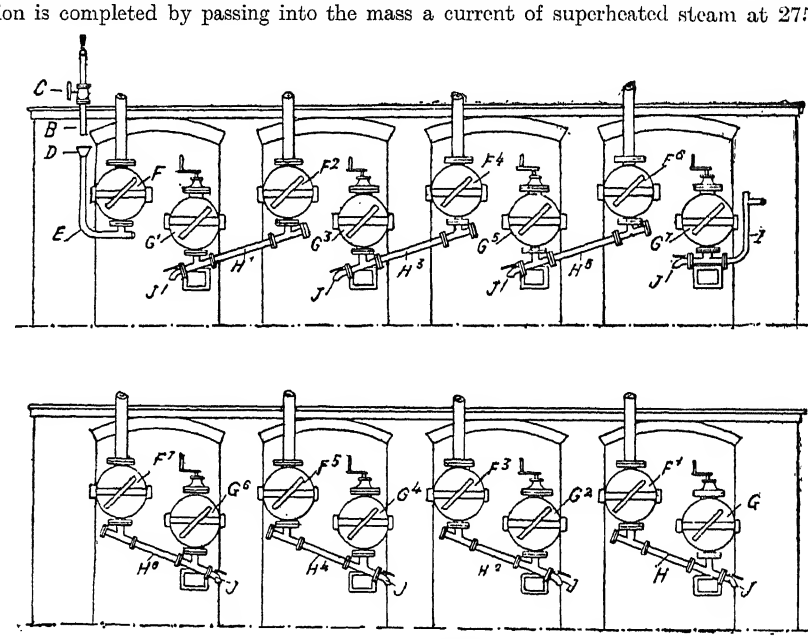


Fig. 435.

With a still holding 300 to 400 quintals, each distillation (including charging and discharging) lasts about four days. Distillation in a vacuum saves time, lessens repairs, and gives an improved yield of oil, better pitch, and a smaller deposit of coke, so that it suffices to clean the retorts after 25 or 30 charges.

In large tar distilleries, after the temperature in the still has reached 270°, the distillation is completed by passing into the mass a current of superheated steam at 275°, the



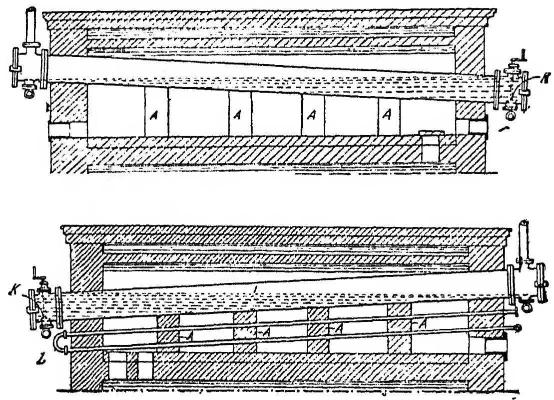
Figs. 436-437.

products boiling at higher temperatures being thus distilled unaltered and a harder pitch obtained; if a soft pitch is desired, heavy oil is introduced into the boiler at the end of the distillation.

Various systems of continuous distillation have been introduced to economise plant, fuel and labour. In the Lenhard process the washed and dried tar, heated to 100°, is forced slowly (70 tons per 24 hours) through a weldless iron coil about 800 metres in length, heated in a furnace by means of producer gas. The temperature of the tar may reach 350°

and, as the mass passes from the coil to a separating vessel, the hot pitch separates and the remainder is transformed instantly into vapours, which are condensed in several successive coils.

In the Hirzel system the whole distillation is effected continuously in a current of superheated steam, only the final products being distilled by direct fire heat from a still



FIGS. 438-439.

connected with the first one. In this way the different oils distil at temperatures lower by 125° to 150° than in the ordinary apparatus, and, hence, are not only less highly coloured, but are also obtained in better yields.

In the Ray system, five or more cylindrical iron retorts are arranged parallel, but alternately, with one extremity high and the other low (Figs. 436—439). The tar from a raised tank enters at the bottom of the first boiler and passes out at the top to enter the second boiler at the base, and so on. The furnace gases heat the last boiler first, so that this attains the highest temperature and the first boiler the lowest temperature. The vapours from the different boilers are condensed in separate coils.

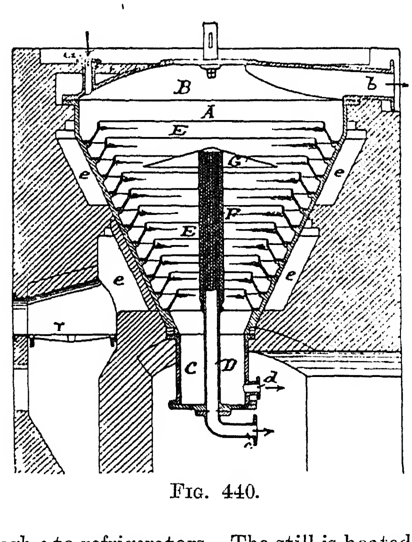


FIG. 440.

Wernecke (Ger. Pat. 301,372, 1907, and 237,823, 1911), has proposed the use of a conical, stepped still, *A*, fitted with a number of superposed peripheral channels, *E*, inside (Fig. 440). The cover, *B*, is fitted with a vapour outlet, *b*, and a pipe, *a*, for the continuous introduction of the tar (which first passes through a heater, where the water and light oils are distilled). The latter enters the uppermost channel, *E*, and overflows into the lower channels, gradually diminishing in volume owing to the distillation of various products; the more or less liquid pitch is discharged at *d*. The vapours of the medium oils pass through the upper orifice, *b*, to refrigerators, but those of the heavy oils from the lower channels are collected by the perforated pipe, *DF*, which is provided with a cap, *G*, and is surrounded by metal gauze, and carries them through *c* to refrigerators. The still is heated by the gases from the hearth, *r*, which circulate in the flues, *e*. The distillation is interrupted only once in 4 to 8 weeks to allow of the removal of the coke deposited on the inner surface of the still. Although the total capacity of the channels is only 600 kilos of tar, the daily output is equal to that of a still of the old type holding 2500 to 3000 kilos. Such a still also serves well for the distillation of *lubricating oils* from petroleum residues.

PRODUCTS OF THE DISTILLATION OF COAL TAR. The products which distil below

110° at ordinary pressure (sp. gr. 0·900 to 0·910) are somewhat similar to the ammoniacal liquor of gasworks, and consist of a more or less coloured liquid on which floats an oil containing a little benzene and toluene.

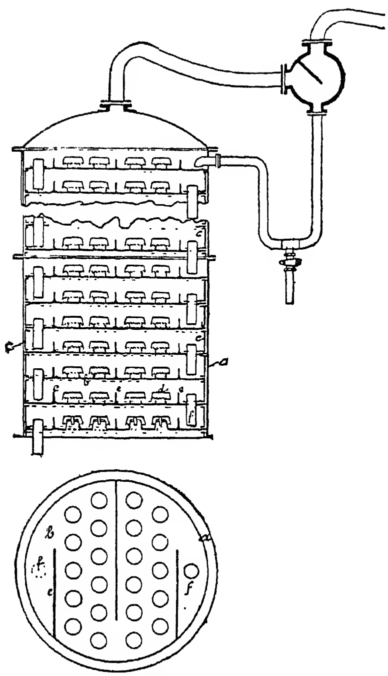


FIG. 441.

The second portion (3 to 5 per cent.) which is collected is that distilling between 110° and 170°, this forming the so-called *light tar-oils* (sp. gr. 0·910 to 0·950).

From 170° to 230° the *phenols* or *medium oils* or *creosote oils* (6 to 9 per cent.) are collected. The next fraction (25 to 30 per cent.) consists of *heavy oils* (up to 270°; sp. gr. 0·980 to 1·030), and the final one, the *anthracene oil* (7 to 9 per cent.) passes over at 270° to 320° (sp. gr. 1·050 to 1·095) and forms a buttery mass composed of oils and crystalline substances. The final residue constitutes the *pitch.*

The percentage amounts of the different products obtained from tar are, on the average, as follows: benzene, about 0·6; toluene, 0·4; homologues of toluene, 0·5; crude phenol, 1; higher phenols, 4 to 5; pyridine bases, 0·2; naphthalene, 7 to 10; heavy oils, 23 to 26; anthracene, 0·3; phenanthrene, 0·6; pitch, 55 to 60; ammonia liquor, 4; gas, about 1·5.[1]

The various fractions obtained in the first distillation of tar are treated as follows:

(A) The **LIGHT OILS** are brownish-yellow and darken in the air and light. Their composition varies with the quality of the tar, as is shown by the following results obtained in actual practice:

	Gasworks tar.		Coke-oven tar.
Crude benzene I. (distilled up to 135°) .	36·12 per cent.	..	12·66 per cent.
,, ,, II. (distilled at 135° to 165°)	15·59 per cent.	..	16·42 per cent.
Phenol oils (165° to 195°)	18·01 per cent.	..	18·47 per cent.
Residue (medium oils)	26·51 per cent.	..	49·36 per cent.
Water and loss	3·67 per cent.	..	3·09 per cent.

The light oils are distilled and rectified in a column apparatus (Fig. 441) with stills holding 100 to 200 quintals and heated by direct-fire or by superheated indirect steam; the first three fractions (up to 195°) are collected separately. The crude benzenes I. and II. can be purified from the small amount of phenols they contain by washing with caustic soda solution; the remaining benzene is then rectified again in order to remove the toluene, of which it may contain as much as 25 per cent. (*see later,* Benzene). The phenol oils (distilled between 165° and 195°) contain appreciable quantities of naphthalene, and are therefore worked up with the medium oils.

(B) **MIDDLE** or **CREOSOTE OILS** vary in amount from 5 to 10 per cent. according to the type of tar used and to the temperature of distillation (110° to 180°). They are brown, and at the ordinary temperature become pasty owing to the separation of naphthalene crystals. They darken in the air and on distillation give the following components:

[1] In a large German coke-tar distillery, where retorts holding 350 quintals were used, the mean yields of several years were as follows: Ammoniacal liquor, 4·27 per cent.; light oils, 4·06; medium oils, 10·38; heavy oils, 6·11; anthracene oil, 13·71; pitch, 60·49; loss, 0·98. The tar distilled contained on an average 24 per cent. of matter (carbon) insoluble in benzene, and the mean cost of distilling 1000 kilos of tar was as follows: Labour, 7·7*d.*; coal (at 1*s.* 7*d.* per quintal), 14·4*d.*; steam, 4·8*d.*; various materials, 1·4*d.*; repairs, 3·8*d.*; depreciation, 11·5*d.*; total, 43·6*d.* In a large distillery fitted with retorts holding 180 quintals and working at reduced pressure a larger annual output was attained, while the mean cost per ton distilled was 36·5*d.*; the yields were as follow: Ammoniacal liquor, 3·86 per cent.; light oils, 1·24; medium oils, 12·02; heavy oils, 8·50; anthracene oil, 18·68; pitch, 54·56; loss, 1·14. When tar free from water is distilled the consumption of coal is diminished from 7·5 to 5 per cent.

	Medium tar-oils	
	Gas	*Metallurgical coke*
Crude benzene II. (to 165°)	4·15 per cent.	1·78 per cent.
Phenol oils (165° to 195°)	21·77 ,,	19·91 ,,
Naphthalene oil (195° to 280°)	43·45 ,,	28·68 ,,
Residue	26·91 ,,	48·18 ,,
Water and loss	3·72 ,,	1·45 ,,

(C) **HEAVY OILS** constitute 25 to 30 per cent. of the tar and form a semi-solid, blackish mass, that obtained from gas (metallurgical coke) tar containing about 28 (30) per cent. of naphthalene and 16 (10) per cent. of phenols. They are fractionally distilled, the main middle fraction being either used directly for various purposes [1] or distilled in a vacuum.

[1] *Heavy tar-oil*, when not redistilled in a vacuum to recover the anthracene, is used as an illuminant, or for the manufacture of lighting gas, or as fuel, or for impregnating wood. To obtain illuminating gas the oil is run in a thin stream into heated iron retorts (as in the cracking of petroleum, *see* p. 87), carbon and an oil still containing a considerable proportion of benzene being formed in addition to the lighting gas.

When these oils are used directly for heating purposes, they are pulverised under the furnaces by means of a steam-jet which introduces the necessary quantity of air.

At the Deutz gas-engine works (near Cologne), heavy tar-oil has been applied in Diesel engines. Tar itself may be used in these engines, especially that from vertical furnaces, which contains far less naphthalene (2 to 3 per cent.) than that from horizontal or inclined gas retorts; the lower the temperature at which coal is distilled the greater is the proportion of paraffin hydrocarbons obtained.

A considerable amount of heavy tar-oils is used for the *disinfection and deodorisation of urinals;* continuous rinsing of these with water may be replaced with advantage by brushing on a thin layer of a mixture of tar-oils of various compositions (heavy tar-oils mixed with heavy mineral oil, soap, etc.). This mixture should answer the following requirements: sp. gr. 0·990 at most; b.-pt. 165° at least; it should remain liquid at 0° and should not separate into different layers on standing; it should not contain soap, alcohols, or free alkalis or mineral acids; at least 75 per cent. should distil at 350°; it should contain at least 7 per cent. of cresol.

Very large quantities of heavy oils are now used for the *preservation of wood.* Timber, railway sleepers, telegraph poles, etc., especially when in contact with the ground, are injured and become unusable in a few years owing to the attacks of various moulds and micro-organisms (*Merulius lacrimans, Polyporus vaporarius, etc.*). Even when hard wood is used it gradually becomes considerably attacked. Telegraph poles and railway sleepers have been successfully treated by smearing with pitch or bitumen the parts which come into contact with the earth, and superficial charring of the wood at the points most subject to attack has also been tried. Formerly much use was made of the method of mineralising wood. Concentrated and more or less hot solutions of various salts (ferrous or copper sulphate, zinc chloride, etc.) are forced into the pores of the wood under pressure; or the wood is heated in a large autoclave, which is then evacuated to remove all the air and water from the pores and subsequently filled with the salt solution, which thus impregnates the wood completely. The process which gives the best results and has become widely used in recent years is, however, that of Bethell, which consists in the complete impregnation of the timber with heavy tar-oils (crude creosote oil); these contain phenols, cresols, etc., which have a marked disinfecting action. In Italy this process has been applied for some years, and is carried out, not in autoclaves, but in open vessels, such as are used in America, the treatment being completed in zinc solutions according to the improvements of the Giussani patents. The beams are first immersed for 5 to 6 hours in a bath of fused masut (*see* p. 86) kept at 160° to 170°, by which means the wood is deprived of its air and water and sterilised; they are then passed into a cold vessel containing medium tar-oil (the portion distilling at 210° to 240° and having an acidity of 25 per cent. due to various phenols) where, after 20 to 30 minutes' cooling, the oil penetrates the pores to a depth of 1 cm. or more. The wood is finally left for 3 to 4 hours in a cold, concentrated solution of zinc chloride, which forces the oil further in and forms a thin superposed layer in the pores (the wood absorbs as much as 15 per cent. of the zinc chloride solution). Thus treated, wood resists the action of weather, water, and soil for 15 to 20 years, soft wood being as resistant as hard.

The German railways require that every sleeper, 2·7 × 0·26 × 0·16 metres, shall contain 7 kilos of creosote oil. In order to economise tar-oil, Ruping's process is often used. This consists in creating an air pressure of 5 atmos. in the autoclave containing the wood and then introducing the creosote oil at 10 atmos. pressure. When the pressure in the autoclave subsequently falls off, the excess of oil is forced out by the air compressed in the pores, the latter remaining coated inside with a thin layer of oil. In this way 2 kilos of creosote oil give the same sterilising effect.

Tar-oils freed from the phenols have a bactericidal effect three times that of zinc chloride, especially if they are emulsified with about 6 per cent. of resin soap and then diluted with 40 times

(D) **ANTHRACENE OIL** or green oil, obtained in the direct distillation of tar, is a dense, almost buttery, greenish-brown mass of specific gravity 1·09 to 1·125, fluid at 60°. It contains 6 to 10 per cent. of crude anthracene (40 per cent. of anthracene), besides naphthalene, methylnaphthalene, phenanthrene, acenaphthene, diphenyl, methylanthracene, pyrene, chrysene, retene, fluorene, fluoranthrene, benzerythrene, carbazole, acridine, about 6 per cent. of higher phenols, α- and β-naphthols, and various basic substances.

The anthracene oil is usually collected in two fractions, I. and II. Anthracene oil I., with specific gravity up to 1·100, is used for the preparation of anthracene, and anthracene oil II. either for making oil gas (*see* p. 64), or lamp-black, or for removing the naphthalene from coal gas (*see* p. 47), or for making *carbolineum*, which is used to preserve and stain wood.

(E) **PITCH** is the final residue of the direct distillation of coal tar (or peat or lignite tar) and forms about 50 to 55 per cent. of the tar.

According to whether the pitch (residue) is required to be more or less liquid or solid, the distillation is suspended after the third or fourth fraction has been collected ; to render the pitch shiny, it is mixed in the still with the heavy oil remaining after the crystallisation of the anthracene.

Soft pitch melts at 50°, medium pitch at about 70° (used in making briquettes from coal residues ; *see* Vol. I., p. 459), and hard pitch, of sp. gr. 1·25 to 1·275, at 90°.

Artificial pitch is made by interrupting the distillation of the tar when the light products have been eliminated and passing a current of air through the liquid at 100°. To render the pitch more readily fusible, it is fused with sulphur.

The percentage elementary composition of pitch is: C, 85 to 92; H, 4·6 to 4·8; O + N + S, 3 to 7 ; ash, 0·5 to 2·5.

Pure carbon remains undissolved when pitch is extracted with tar phenols, but benzene extracts from pitch a *pure bitumen* used in electrotechnics, the insoluble part being employed either to make lamp-black or as retort graphite for making electrodes.

Perkin calculated the value of the final products of the complete and rational treatment of 9,000,000 tons of coal (costing £5,400,000) to be as follows: dyes, £3,350,000 ; ammonium sulphate (195,000 tons), £1,960,000 ; pitch (325,000 tons), £365,000 ; creosote oil (1,125,000 hectols.), £208,000 ; crude carbolic acid (45,000 hectols.), £220,000 ; coke £2,400,000. Total, £8,503,000, exclusive of the 30 cu. metres of gas per ton of coal carbonised.

BENZENE (or **Benzol**), C_6H_6. This was discovered by Faraday in 1825 in the liquid obtained on compressing illuminating gas, but the more abundant source, tar, was found by Hofmann in 1845.

It is obtained pure by the dry distillation of benzoic acid with lime, and then forms a colourless, mobile, highly refractive liquid of sp. gr. 0·8841 at 15°, b.-pt. 80·4° (a mixture of 60·65 parts of benzene with 39·35 of methyl alcohol boils unchanged at 58·35°), and m.-pt. + 5·4° ; it burns with a luminous, smoky flame.

The calorific value of benzene is 10,050 cals. per kilo, the latent heat of evaporation being 94·4 cals., and the vapour pressures at different temperatures as follows :

Temperature	− 10°	0	10	20	30	40	50	60	70	80	90	100
Mm. of Mercury	14·8	26·5	45·4	74·7	118·2	181	269	388·6	547·4	753·6	1016	1344

The commercial product contains thiophen and traces of carbon disulphide, which may be eliminated in various ways, *e.g.*, with moist ammonia (Schwalbe, Ger. Pat. 133,761) which separates insoluble oil drops, or by boiling with mer-

their weight of water ; less than 1 kilo of tar-oils is thus sufficient for a railway sleeper. Good results have also been obtained with heavy petroleum oils heated to 200° with 2 per cent. of sulphur and then mixed with 40 per cent. of creosote oil.

According to Friedmann and Heidenstam, wood is preserved well by impregnating it with calcium cresolate (soluble in water) and then precipitating calcium carbonate and cresol in the pores by simple exposure of the wood to air or, better, to fumes rich in carbon dioxide (Danish Pat. 12,419 of 1909). Injection of a hot solution of zinc β-naphthalenesulphonate, which is insoluble in the cold, has also been suggested.

curic acetate, sulphur chloride, or 0·5 per cent. of aluminium chloride; according to Ger. Pat. 211,239, formaldehyde, acetaldehyde, or phthalic anhydride may also be used, all these substances combining with thiophen. Benzene dissolves resins, fats, sulphur, rubber, gutta-percha, camphor, etc., it mixes with alcohol, ether, acetone, etc., and is almost completely insoluble in water.

The preparation of *artificial benzene*, starting with petroleum, was described on p. 87. Benzene forms the prime material for many varied syntheses of aromatic compounds, such as nitrobenzene, aniline, phenol, etc., and of dyes (also nowadays of artificial indigo). In presence of $AlCl_3$ it is rendered more active chemically, as though it contained a true double linking. It is used as a solvent for fats and for purifying many organic compounds; the addition of 15 per cent. of benzene to the alcohol used with an Auer mantle for lighting purposes results in a saving of 27 per cent. of the alcohol. Large quantities of 90 per cent. benzene are now used for carburetting illuminating gas to which water-gas has been added (*see* p. 58). It is also employed for dissolving rubber and lacs for making linoleum, for removing fat from bones, and for automobile engines, but should contain toluene to prevent it from freezing in winter.

At one time it was obtained exclusively from gas-tar, this yielding also larger quantities of toluene, the uses of which were limited. After 1880, when the tendency was to obtain increased yields of illuminating gas by raising the temperature of carbonisation of the coal, the quantity of tar diminished, as also, in still greater proportion, did the amount of benzene. In 1882, the price of benzene, then in great demand by dye manufacturers, exceeded £12 per quintal. It was then that attention was turned to the recovery of the tar from metallurgical coke factories, but although this tar is obtainable in large amounts, it is very poor in benzene, most of which escapes with the gases and is wasted in the furnaces. Darby was the first to suggest the recovery of the benzene from the gases of the coke furnaces; and nowadays these gases, before being burnt, are either strongly cooled to condense the benzene or washed with slightly volatile tar-oils, in which the benzene dissolves and from which it is recovered by subsequent heating (*see* Note, p. 58).[1] As a

[1] Benzene is now recovered from its solutions in heavy mineral or tar-oils by means of the Kubierschky rectifying column (Ger. Pat. 194,567, 1906), which works continuously and gives a sharper separation of the components of a mixture than other systems. The action of this column is based on the displacement of a vapour or gas by superposition of another lighter vapour or gas; the two layers do not mix if the velocity of movement is less than 0·75 metre per second, and usually the velocity in such an apparatus is 0·3 metre per second.

In the ordinary rectifying column (*see* p. 158) the mixed vapour (for instance, of alcohol and water) passes upwards and has to overcome the resistance of the liquid layers in the chambers above; further, the lighter, hotter and less concentrated vapours below do not merely displace the cooler, heavier and more concentrated vapours of the upper chambers, but mix with them to some extent and render the rectification less perfect. In the Kubierschky column, however, the lighter vapour passes from the lower part of one chamber to the upper part of the chamber above and settles gently on the heavier and colder vapour contained therein, this being thus forced to the upper part of the chamber above (*see* Fig. 442). The dilute alcoholic liquid enters half way up the column by the pipe *a* and descends as a spray through the perforated plates of chambers 6, 5, and so on. At the same time steam at slightly above 100° enters by *b* into chamber 1 and descends along with the spray of alcoholic liquid from the perforated base of chamber 2. This liquid gives up to the steam any traces of alcohol it still contains and is discharged from the perforated bottom of chamber 1 through the pipe *d*. The steam passes into the upper part of chamber 2 and there forms a layer above the slightly more alcoholic (and hence heavier) vapour therein and forces this into the top of chamber 3, and so on. The ascending vapours are not subjected to friction, since they fall with the liquid spray and never bubble through liquid layers. At the top of the column, in chamber 14, the vapour rich in alcohol rises through the pipe *e* to the dephlegmator, *B* (acting as a preheater for the dilute alcoholic liquid entering the column at *a*), where a little water and a very little alcohol condense and fall as spray into chamber 14 and the lower chambers. The alcohol-rich vapour not condensed in the dephlegmator issues through the pipe *c* and is condensed in a coil a short distance away. The column is composed of a number of flanged cast or wrought-iron rings or elements bolted together.

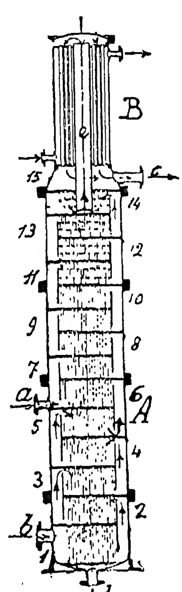


FIG. 442.

Communication between the lower part of one chamber and the upper part of the chamber

result of this process, the production of benzene became more than ten times that of *toluene*, the price, which was £2 to £3 per quintal in the period 1885–1896, falling to 20*s.* to 24*s.* in 1898–1910, and to below 16*s.* in 1913. Pure thiophen-free benzene cost before the War about 1*s.* 6*d.* per kilo and the puriss. product, obtained from benzoic acid, 32*s.* per kilo.

Various forms of apparatus are used for distilling and rectifying crude benzene, all being heated by means of indirect steam. Use may be made of Hirzel's apparatus (p. 88), or of the similar one of Heckmann (p. 165), but having a still with a smaller base in the form of a short, horizontal cylinder and with a dephlegmator in the upper part of the column.[1]

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above is effected by means of various arrangements, for example, by tubes, as shown in Fig. 443, or by means of a central tube and a peripheral annular space (Fig. 444). The liquid collecting on the bottom of each chamber passes into the chamber beneath through hydraulically sealed bells, passage of the vapour through the bases of the chambers being thus prevented. The fall

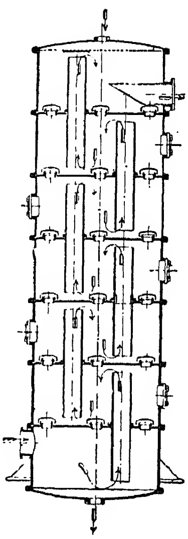

Fig. 443.

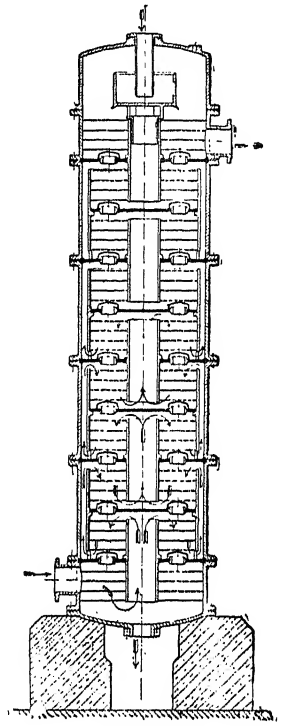

Fig. 444.

of the spray may be rendered slower by the insertion in the chambers of perforated plates or metallic gauze (Fig. 444).

For the recovery of benzene from its solutions in heavy oils use may be made of two such columns superposed. In the lower one the solution, falling as a spray, comes into contact with steam which removes the benzene, the mixed water and benzene vapours then passing upwards through the upper column, where they meet a spray of crude benzene. The mixed water and benzene vapours issuing from the top of this column are condensed and the water separated by decantation.

[1] The different fractions obtained on rectification are as follows: (1) *commercial 90 per cent. benzene I.* of sp. gr. 0·885 at 15° (90 per cent. of this distils at 100° and 100 per cent. at 120°; it contains about 20 per cent. of toluene; 120° is termed the *dry-point* of the benzene); (2) *50 per cent. benzene II.* with sp. gr. 0·880 (50 per cent. of this distils at 100° and 90 per cent. at 120°); (3) *heavy benzene* or *solvent naphtha* with sp. gr. 0·875 (20 per cent. of this distils at 130° and 90 per cent. at 160°; it serves as a good solvent for rubber).

The *testing of commercial benzene* is carried out by determining its density and by fractionally distilling it; 100 c.c. are distilled in an ordinary flask with a side-tube (*see* p. 75) and heated on a metal gauze with a flame so adjusted that two drops distil over per second; the flame is removed for a minute before changing the cylinders in which the separate fractions (100°, 120°, 130°, 160°) are collected. In some cases a nitration test is made, note being taken of the yield of nitrobenzene, purified by steam and then rectified (*see later*, Nitrobenzene). The

PURE BENZENE, now required in considerable quantities for various chemical industries, such as the manufacture of synthetic phenol (*see later*), the manufacture of nitrobenzene for making pure aniline, etc., is obtained from purified 90 per cent. benzene. This is washed several times with a total of 2 to 3 per cent. of 96 to 98 per cent. sulphuric acid or of 2 per cent. of oleum. After standing for some time, it is washed first with a little water and then with 18 per cent. caustic soda solution (0·4 per cent. of NaOH calculated on the weight of the benzene), and afterwards subjected to careful fractional distillation, being heated by indirect steam. The fraction boiling at 80° to 85° is further rectified, and then yields 99·5 per cent. benzene, b.-pt. 80·2° to 80·8° at 760 mm. pressure; a variation of 1 mm. in the pressure alters the boiling-point by about 0·05°.

The final purification of small quantities of benzene may be effected by cooling the liquid until it freezes and then squeezing or centrifuging away the toluene, etc., from the crystals.

When shaken with an equal volume of pure concentrated sulphuric acid, pure benzene should not turn the acid yellow. If traces of *thiophen* are present, the benzene will give the blue colour of indophenin when treated with isatin and concentrated sulphuric acid.

TOLUENE (or Methylbenzene), $C_6H_5 \cdot CH_3$, is formed by the dry distillation of balsam of Tolu and of various resins, and is obtained in appreciable quantities by the distillation of tar (*see above*). It boils at 110·4°, does not solidify even at — 28°, and has the sp. gr. 0·87 at 15°. It occurs to the extent of 10 to 15 per cent. in crude benzene I. and of 25 per cent. or more in crude benzene II.

Crude toluene is purified from the hydrocarbons of the fatty series which always accompany it (and are not eliminated by rectification) by washing it with hot sulphuric acid containing a little nitric acid, the olefines being thus polymerised and the thiophen decomposed. It may also be purified by heating with sodium.

Commercial pure toluene gives 99 per cent. of distillate below 112° and 95 per cent. between 108° and 110° (two drops per second). It does not colour on protracted shaking with concentrated sulphuric acid, and if 90 c.c. of toluene and 10 c.c. of nitric acid (44° Bé.) are shaken together for some minutes in a tall glass-stoppered cylinder, the nitric acid should become only a transparent red and not a greenish black and should not thicken.

Toluene is used in the manufacture of dyes, pharmaceutical products, perfumes, etc., and, during recent years, of trinitrotoluene (*see later*), which is used in large quantities as an explosive.

XYLENES (Dimethylbenzenes), $C_6H_4(CH_3)_2$. Xylene obtained from tar contains the three isomerides, *o*-, *m*-, and *p*-, metaxylene being present to the extent of 70 to 80 per cent. They cannot be separated by fractional distillation owing to the small differences between their boiling-points (*o*- 142°; *m*- 139°; *p*- 138°).

Treatment with concentrated sulphuric acid in the cold, however, converts the *o*- and *m*- compounds into the corresponding sulphonic acids, the *p*-xylene remaining unchanged. The sodium salt of *o*-toluenesulphonic acid crystallises more readily than that of the *m*-compound, so that the three hydrocarbons can be separated. With oxidising agents, the xylenes give phthalic acids (*see later*).

It is mostly *m*-xylene which is used in the manufacture of dyes.

ETHYLBENZENE, $C_6H_5 \cdot C_2H_5$, is obtained by Fittig's synthesis (*see* p. 622) and gives benzoic acid on oxidation (difference from the xylenes).

TRIMETHYLBENZENES, $C_6H_3(CH_3)_3$ (*see* Table, p. 623). The following isomerides are known:

(*a*) Mesitylene (symm. 1 : 3 : 5-) is a liquid of pleasant odour boiling at 165°. Its constitution is proved by its synthesis from acetone or allylene, by the fact that it does not form isomeric compounds by further substitution in the nucleus, and by its oxidation products: nitric acid oxidises the three side-chains successively and chromic acid simultaneously.

(*b*) Pseudocumene (asymm. 1 : 2 : 4-) is prepared from bromo-*p*-xylene (1 : 4 : 2) or bromo-*m*-xylene (1 : 3 : 4) by Fittig's synthesis, which indicates its constitution. It is obtained in small proportion from the distillation products of tar, and is separated from mesitylene by conversion into the slightly soluble sulphonic acid (*see* Xylenes).

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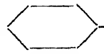
addition of petroleum spirit to benzene is detected by the lowering of the density; also petroleum spirit does not dissolve tar-pitch or picric acid, which are readily soluble in benzene. Further, the latter reacts vigorously with concentrated nitric acid, which does not attack petroleum spirit.

(*c*) *n*-Propylbenzene, $C_6H_5 \cdot CH_2 \cdot CH_2 \cdot CH_3$. The constitution of this compound is shown by the facts that it yields benzoic acid when oxidised and that it is obtained synthetically (Fittig) from propyl iodide and bromobenzene or from benzyl chloride, $C_6H_5 \cdot CH_2Cl$, and zinc ethyl.

(*d*) Isopropylbenzene (or *cumene*), —$CH(CH_3)_2$, also gives benzoic acid on oxidation, and is formed from benzene with either isopropyl iodide or normal propyl iodide (in the latter case aluminium chloride is necessary to cause molecular rearrangement); it is obtained also on distilling cuminic acid, $C_6H_4(C_3H_7) \cdot CO_2H$, or by the interaction of benzylidene chloride, $C_6H_5 \cdot CHCl_2$, and zinc methyl.

TETRAMETHYLBENZENES, $C_6H_2(CH_3)_4$. The best known of these are the following:

(*a*) Durene (1 : 2 : 4 : 5) or *s*-tetramethylbenzene, which is found, together with isodurene, in tar; it is a solid, has a smell resembling that of camphor, and is prepared synthetically from toluene and methyl chloride.

(*b*) and (*c*) Isodurenes, two isomerides being known (1 : 2 : 3 : 4 and 1 : 2 : 3 : 5) (*see* Table, p. 623).

(*d*) *p*-Methylisopropylbenzene or *cymene*, CH_3—$CH(CH_3)_2$, is a liquid of pleasant odour, b.-pt. 185°. It occurs naturally in cumin oil (from *Cuminum cyminum*) and in various essential esters, and it can be prepared by heating camphor with phosphoric anhydride or by the interaction of oil of turpentine and iodine. On oxidation it yields various acids.

(*e*) *m*-Isocymene is found in resin oil.

Hexamethylbenzene (*mellithene*), $C_6(CH_3)_6$, m.-pt. 164°, is a stable compound and can be neither nitrated nor sulphonated, owing to the absence of hydrogen atoms from the nucleus. When oxidised with potassium permanganate, it gives Mellitic Acid, $C_6(CO_2H)_6$.

HYDROCARBONS WITH UNSATURATED SIDE-CHAINS

As far as the nucleus is concerned, these compounds behave like true benzene derivatives, whilst by means of the unsaturated side-chain they give all the reactions of unsaturated methane derivatives.

STYRENE, $C_6H_5 \cdot CH : CH_2$, occurs in storax and is formed on heating cinnamic acid, which loses CO_2 :—$C_6H_5 \cdot CH : CH \cdot CO_2H = CO_2 + C_6H_5 \cdot CH : CH_2$. It is a liquid of pleasant odour boiling at 146°, and tends to polymerise to Metastyrene. Styrene combines with bromine, iodine, hydrogen, etc., in the same way as olefines do. When it is treated with nitric acid, a nitro-group is introduced into the side-chain, giving Nitrostyrene, $C_6H_5 \cdot CH : CH \cdot NO_2$, the constitution of this being shown by its formation from benzaldehyde and nitromethane: $C_6H_5 \cdot CHO + CH_3 \cdot NO_2 = C_6H_5 \cdot CH : CH \cdot NO_2 + H_2O$.

Styrene serves for the synthesis of anthracene (*q.v.*).

PHENYLACETYLENE, $C_6H_5 \cdot C ⋮ CH$, is a liquid of pleasant odour boiling at 142°, and is prepared by converting acetophenone, $C_6H_5 \cdot CO \cdot CH_3$, by means of PCl_5, into the dichloro-derivative, $C_6H_5 \cdot CCl_2 \cdot CH_3$, and eliminating 2HCl from the latter by the action of potassium hydroxide.

It is also obtained by the cautious distillation of Phenylpropiolic acid, $C_6H_5 \cdot C ⋮ C \cdot CO_2H$. Like acetylene, it forms metallic compounds; treatment with concentrated sulphuric acid results in the addition of H_2O, subsequent dilution with water giving acetophenone.

B. HALOGEN SUBSTITUTION PRODUCTS OF BENZENE

Halogens act on benzene and its homologues, replacing one or more atoms of hydrogen and forming colourless liquids (sometimes crystalline substances) which are heavier than water, distil unchanged, and dissolve in alcohol and in ether.

In aromatic hydrocarbons, a halogen in the benzene nucleus is held much more firmly than one in a side-chain and cannot be replaced by hydroxyl by the action of silver hydroxide or by the amino-group by treatment with ammonia; only by sodium or sodium alkoxide at about 200° can the halogen be eliminated.

The chlorine in the nucleus of chlorotoluene is united as firmly as in chlorobenzene, whilst the chlorine in benzyl chloride is readily replaceable, just as is the case with that in methane derivatives. To ascertain whether the halogen is present in the nucleus or in the side-chain, the oxidation products are studied; thus, chlorotoluene gives chlorobenzoic acid, $C_6H_4Cl \cdot CO_2H$, whilst benzyl chloride yields benzoic acid.

For distinguishing isomeric halogen derivatives, the same methods are used as for the xylenes, etc.

In order to be able to name aromatic derivatives the more readily, the following names are given to the more common of the different groups or *aromatic residues* (known as aryl radicals and denoted generally by Ar): —OH, phenolic; $—CO_2H$, carboxyl; $—O \cdot CH_3$, methoxy; $—C_6H_5$, phenyl; $—CH_2 \cdot C_6H_5$, benzyl; $—CO \cdot C_6H_5$, benzoyl; —CN, nitrile; $—SO_3H$, sulpho or sulphonic; $\vdots C \cdot C_6H_5$, benzenyl; $C_6H_4\left\langle {C= \atop CO} \right\rangle O$, phthalyl; $: CH \cdot C_6H_5$, benzylidene or benzal; $—C_6H_4 \cdot C_6H_4—$, diphenylene.

GENERAL METHODS OF FORMATION. (1) In direct sunlight, chlorine and bromine act on benzene, giving additive products, *e.g.*, $C_6H_6Cl_6$ and $C_6H_6Br_6$, but in diffused light (best in presence of traces of iodine, aluminium chloride, antimony trichloride, etc.), substitution products are formed. With homologues of benzene, if the reaction is carried out in the cold and in the dark (or in diffused light) or in presence of iodine (which acts catalytically), the halogen enters only the benzene ring (even in the hot, if iodine is present), whilst in the hot or in direct sunlight, the substitution takes place principally in the side-chain.

(2) By heating halogenated acids with lime:

$$C_6H_4Cl \cdot CO_2H = C_6H_5Cl + CO_2.$$

(3) By withdrawing oxygen from oxygenated compounds (phenols, aromatic alcohols, ketones, acids, aldehydes) by means of PCl_5; *e.g.*, $C_6H_5 \cdot OH + PCl_5 = POCl_3 + HCl + C_6H_5Cl$.

(4) By boiling with cuprous chloride or potassium iodide the diazo-compounds obtained from the corresponding nitro- or amino-compounds: $C_6H_5N : NCl = C_6H_5Cl + N_2$; $C_6H_5N : NCl + KI = KCl + N_2 + C_6H_5I$.

(5) Iodo-derivatives may be obtained by the action of iodine, iodic acid being added to oxidise the hydriodic acid which is formed. They are, however, usually obtained by process (4).

(6) *Iodobenzene*, C_6H_5I, unites with two atoms of chlorine, forming *iodosobenzene chloride*, $C_6H_5ICl_2$, digestion of which with alkali yields *iodosobenzene*, $C_6H_5I : O$, the latter, when heated or oxidised (with chloride of lime) giving *iodylbenzene*, $2C_6H_5IO = C_6H_5I + C_6H_5IO_2$ or $C_6H_5IO + O = C_6H_5IO_2$ (an explosive, crystalline compound).

Chlorination or bromination of *toluene* yields the *para*- and *ortho*-derivatives in equal quantities; the *meta*-derivative is obtained indirectly (from diazo-compounds).

BENZYL CHLORIDE, $C_6H_5 \cdot CH_2Cl$, is a colourless liquid with a pungent odour, melting at $-49°$ and boiling at 178°; its specific gravity at 15° is 1·113. It was first prepared by Cannizzaro in 1853, and is obtained by chlorinating boiling toluene. With potassium acetate this chloride gives the acetyl-derivative, with potassium hydrosulphide a mercaptan, and with ammonia amino-bases. On protracted boiling with water it is transformed into benzyl alcohol, while boiling with lead nitrate converts it into benzaldehyde; when heated with finely divided copper, it loses chlorine and condenses to dibenzyl, $C_6H_5 \cdot CH_2 \cdot CH_2 \cdot C_6H_5$.

It is used for the preparation of oil of bitter almonds and for numerous aromatic syntheses its chlorine atom being readily replaceable.

Benzyl bromide, when treated with potassium iodide, gives **Benzyl iodide.** These

PRINCIPAL HALOGEN DERIVATIVES OF BENZENE

Empirical formula	Name	Melting-point	Boiling-point	Specific gravity
	Chloro-derivatives			
C_6H_5Cl	Monochlorobenzene	$-45°$	$+132°$	1·128 at 0°
$C_6H_4Cl_2$	*o*-Dichlorobenzene (1 : 2)	—	179°	
	m- „ (1 : 3)	—	172°	
	p- „ (1 : 4)	$+53°$	172°	
$C_6H_3Cl_3$	*v*-Trichlorobenzene (1 : 2 : 3)	16°	218°	
	as- „ (1 : 2 : 4)	63°	213°	
	s- „ (1 : 3 : 5)	54°	208°	
$C_6H_2Cl_4$	*v*-Tetrachlorobenzene (1 : 2 : 3 : 4)	46°	254°	
	as- „ (1 : 2 : 3 : 5)	50°	246°	
	s- „ (1 : 2 : 4 : 5)	137°	244°	
C_6HCl_5	Pentachlorobenzene	86°	276°	
C_6Cl_6	Hexachorobenzene	226°	326°	
	Bromo-derivatives			
C_6H_5Br	Monobromobenzene	$-31°$	$+155°$	1·517 at 0°
$C_6H_4Br_2$	*o*-Dibromobenzene (1 : 2)	$-1°$	224°	2·003 at 0°
	m- „ (1 · 3)	$+1°$	220°	1·955 at 20°
	p- „ (1 : 4)	87°	219°	1·841 at 89°
$C_6H_3Br_3$	*v*-Tribromobenzene (1 : 2 : 3)	87°	—	
	as- „ (1 : 2 : 4)	44°	275°	
	s- „ (1 : 3 : 5)	120°	278°	
$C_6H_2Br_4$	*v*-Tetrabromobenzene (1 : 2 : 3 : 4)	—	—	
	as- „ (1 : 2 : 3 : 5)	98°	329°	
	s- „ (1 : 2 : 4 : 5)	175°	—	
C_6Br_6	Hexabromobenzene	above 315°	—	
$C_6H_4Br{\cdot}CH_3$	*o*-Bromotoluene (1 : 2)	$-26°$	181°	1·422 at 20°
	m- „ (1 : 3)	$-39{\cdot}8°$	184°	1·410 at 20°
	p- „ (1 : 4)	$+28°$	185°	1·392 at 20°
$C_6H_5{\cdot}CH_2Br$	Benzyl bromide	liquid	198°	1·438 at 22°
	Iodo-derivatives			
C_6H_5I	Iodobenzene	$-30°$	188°	
$C_6H_4I_2$	*o*-Di-iodobenzene (1 : 2)	$+27°$	286°	
	m- „ (1 : 3)	40°	285°	
	p- „ (1 : 4)	129°	285°	

products are also formed from benzyl alcohol, $C_6H_5 \cdot CH_2 \cdot OH$, and halogen hydracids ; they may be converted back into the alcohol by boiling with water or potassium carbonate solution.

BENZAL or **BENZYLIDENE CHLORIDE**, $C_6H_5 \cdot CHCl_2$, and **Benzotrichloride**, $C_6H_5 \cdot CCl_3$, are obtained either by protracted chlorination of boiling toluene or by the action of PCl_5 or benzaldehyde or benzoic acid.

Benzal chloride boils at 204° and has the sp. gr. 1·295 at 16°, while the trichloride melts at $-22°$, boils at 213°, and has the sp. gr. 1·380 at 14°.

Mixed halogen derivatives are known, as also is **Hexachlorohexahydrobenzene**, $C_6H_6Cl_6$. Numerous halogenated derivatives of unsaturated aromatic hydrocarbons have likewise been prepared, *e.g.*, **α-Bromostyrene**, $C_6H_5 \cdot CBr : CH_2$, and **β-Bromostyrene**, $C_6H_5 \cdot CH : CHBr$.

C. SULPHONIC ACIDS

These are formed directly from the aromatic hydrocarbons by the action of concentrated or fuming sulphuric acid or of chlorosulphonic acid, $Cl \cdot SO_3H$. Improved yields are obtained in presence of mercury or ferrous sulphate, which exerts a catalytic action.

They are crystalline substances, readily soluble in water and even hygroscopic, and are separated from the excess of sulphuric acid either by means of their calcium or barium salts, which are soluble, or by saturation of the aqueous solution with sodium chloride and subsequent cooling; in the latter case, the sodium sulphonate separates, this being decomposed with the calculated quantity of a mineral acid and the free sulphonic acid extracted with ether.

When treated with superheated steam or with hydrochloric acid, they lose the sulphonic group, the aromatic hydrocarbon being thus regenerated. With PCl_5 they form the acid chlorides, *e.g.*, $C_6H_5 \cdot SO_2Cl$, which, with ammonium carbonate, yield the *sulphamides*, $C_6H_5 \cdot SO_2 \cdot NH_2$ (*see later*). On energetic reduction, *thiophenol* (phenyl hydrosulphide), $C_6H_5 \cdot SH$, is formed.

BENZENESULPHONIC ACID, $C_6H_5 \cdot SO_3H$, is obtained by the direct action of concentrated sulphuric acid on benzene: $C_6H_6 + H_2SO_4 = H_2O + C_6H_5{\cdot}SO_3H$. Its barium and lead salts being soluble, it can be readily separated from the excess of sulphuric acid.

It is very stable and is not decomposed on boiling with alkali or acid (as is ethylsulphonic acid), but if heated with hydrochloric acid at 150° or with superheated steam in presence of concentrated phosphoric acid, it takes up water, giving benzene: $C_6H_5 \cdot SO_3H + H_2O = C_6H_6 + H_2SO_4$. When distilled with potassium cyanide, it forms benzonitrile, $C_6H_5 \cdot SO_3K + KCN = K_2SO_3 + C_6H_5 \cdot CN$.

When fused with alkali it forms phenol, $C_6H_5{\cdot}SO_3K + KOH = K_2SO_3 + C_6H_5{\cdot}OH$, while with PCl_5 it yields **Benzene sulphochloride,** $C_6H_5{\cdot}SO_3H + PCl_5 = POCl_3 + HCl + C_6H_5{\cdot}SO_2Cl$ (decomposable by water).

With ammonia, ammonium carbonate, or primary or secondary amines, benzene sulphochloride gives more or less substituted **Benzenesulphonamides,** *e.g.*, $C_6H_5 \cdot SO_2 \cdot NH_2$, $C_6H_5{\cdot}SO_2 \cdot NHR$, $C_6H_5 \cdot SO_2 \cdot NR_2$, which crystallise well. As the tertiary amines do not give this reaction, they can be separated from other amines.

Owing to the highly acid character of the SO_2 group, the amino-group does not form salts, but its hydrogen can be replaced by metals, *e.g.*, by dissolving in sodium hydroxide solution. Sulphur trioxide converts benzene into **Sulphobenzide** (*sulphone*), $(C_6H_5)_2SO_2$.

Nitration of benzenesulphonic acid yields mainly *m*-nitrobenzenesulphonic acid, but small quantities of the ortho- and para-derivatives are also formed.

Reduction of *p*-nitrobenzenesulphonic acid yields **Sulphanilic acid** (*p-aminobenzenesulphonic acid*), $NH_2 \cdot C_6H_4 \cdot SO_3H$ (discovered by Gerhardt in 1845), which is also obtained on heating aniline with fuming sulphuric acid or on heating aniline sulphate at 200°. This acid and also the corresponding meta-acid are used in the manufacture of artificial dyestuffs, and both of them can be diazotised (*see later*).

Sulphonic compounds and their salts are of importance in the dye industry as they give dyes soluble in water and readily applicable to the dyeing of textile fabrics.

Polysulphonic acids of benzene and its homologues are also known, some of them serving for the separation of isomeric aromatic hydrocarbons (*see* Toluene).

D. PHENOLS

Phenols contain hydroxyl groups in place of one or more hydrogen atoms of the benzene nucleus. They have a characteristic odour (phenol, thymol), and certain of them are partially soluble in water, while all of them are soluble in alcohol and in ether; they distil unchanged and have a more or less marked antiseptic action.

Their properties resemble, to some extent, those of tertiary alcohols and those of weak acids. Thus, ethers are formed by the action of alkyl halogen compounds on the sodium derivatives of the phenols, anisole, $C_6H_5 \cdot OCH_3$, and phenyl sulphate, $C_6H_5 \cdot O \cdot SO_3H$, being obtained in this way; the latter compound is readily hydrolysed. They are, however, stable towards oxidising agents, nitric acid forming substitution products. The hydroxyl group is with some difficulty replaced by chlorine by the action of PCl_5. They act as weak acids, but with alkalis form stable salts, which are soluble in water, are decomposed even by carbonic acid, and show only slight electrical conductivity.

Halogens and nitric acid replace the benzene hydrogen of phenols more *easily* than that of benzene itself or its homologues, so that even in dilute solution phenol can be precipitated quantitatively as tribromophenol by the action of bromine water.

If the hydroxyl group is joined to a side-chain and not to the benzene nucleus directly, the compound is an aromatic alcohol and not a phenol.

Oxidation of homologues of phenol yields hydroxy-acids, the side-chain being oxidised while the phenolic groups remain intact.

When distilled with zinc dust, phenols give the corresponding aromatic hydrocarbons.

In aqueous neutral solution, phenols give a violet, green, or other coloration with ferric chloride, calcium hypochlorite, or, in some cases, iodine. In general, they exert a reducing action.

With nitrous acid, phenols form isonitroso-derivatives (oximes), and, in presence of concentrated sulphuric acid, intensely coloured solutions are formed which are turned blue by potash (*Liebermann's reaction*). The sodium or potassium derivatives of the phenols (*phenoxides*), with carbonic acid (or $CCl_4 + KOH$) give aromatic hydroxy-acids :

$$C_6H_5 \cdot OH + CO_2 = OH \cdot C_6H_4 \cdot CO_2H.$$

With chloroform and sodium hydroxide, they yield the corresponding aldehydes.

They react with diazo-compounds and various other compounds forming colouring-matters (*see later*). The action of zinc chloride (or calcium chloride) and ammonia on phenols results in replacement of the OH by NH_2.

With formaldehyde they yield characteristic resinous condensation products (*see* Baekelite, p. 641). The commoner phenols are obtained from coal- or wood-tar.

(*a*) MONOHYDRIC PHENOLS

These are found alone or together with polyhydric phenols, and partly in the form of ethers (*e.g.*, guaiacol,$OH \cdot C_6H_4 \cdot OCH_3$, cresol, etc.) in the tar obtained by the dry distillation of wood or coal. They are separated from the tar-oils by means of caustic soda, which renders them soluble, and, after separation, are set free by mineral acid and subjected to fractional distillation.

They are also obtained industrially by fusing salts of sulphonic acids with alkali (in iron vesesls ; in the laboratory silver vessels are used) :

$$C_6H_5 \cdot SO_3K + 2KOH = C_6H_5 \cdot OK + K_2SO_4 + H_2O.$$

If the nucleus contains chlorine atoms, these are also substituted by hydroxyl groups by this reaction.

Phenols are formed by boiling diazo-compounds (*see later*) with water in dilute sulphuric acid solution :

$$C_6H_5 \cdot N_2Cl + H_2O = N_2 + HCl + C_6H_5 \cdot OH.$$

Also, when benzene is oxidised with H_2O_2, or with oxygen in presence of aluminium chloride, phenols are obtained.

Chlorine atoms or amino-groups joined directly to the nucleus may be replaced by hydroxyl-groups by the action of sodium hydroxide, but only when the nucleus contains also strongly negative groups, *e.g.*, NO_2.

PHENOL (Carbolic Acid), $C_6H_5 \cdot OH$, was first discovered by Runge in tar and occurs, to a small extent and in combination, in urine.

It is separated from tar-oils (*see* pp. 628, 629) by treatment with caustic soda solution (sp. gr. 1·09) and agitation by a current of air ; steam is passed through the decanted alkaline solution of phenol, this removing the naphthalene, etc. The phenol is then liberated by H_2SO_4 or CO_2 (*e.g.*, flue gases) and washed several times with water, *crude*

THE MOST IMPORTANT PHENOLS

Formula	Name	Melting-point	Boiling-point	Specific gravity
$C_6H_5 \cdot OH$	Phenol (hydroxybenzene)	+ 42·5°	183°	1·039 at 58·5°
$CH_3 \cdot C_6H_4 \cdot OH$	*o*-Cresol or *o*-hydroxytoluene (1-methyl-2-hydroxybenzene)	30	191	1·043 at 23°
„	*m*- „ „ (1- „ 3- „)	4	203	1·035 at 13·6°
„	*p*- „ „ (1- „ 4- „)	36	202	1·034 at 18°
$(CH_3)_2C_6H_3 \cdot OH$	*o*-Xylenol (*v*) (1 : 2-dimethyl-3-hydroxybenzene)	73	213	—
„	*o*- „ (*as*) (1 : 2- „ 4- „)	65	222	—
„	*m*- „ (*v*) (1 : 3- „ 2- „)	49	—	—
„	*m*- „ (*as*) (1 : 3- „ 4- „)	25	209	1·036 at 0°
„	*m*- „ (*s*) (1 : 3- „ 5- „)	63	218	—
„	*p*- „ (1 : 4- „ 2- „)	75	209	0·971 at 81°
$C_2H_5 \cdot C_6H_4 \cdot OH$	*o*-Ethylphenol (1-ethyl-2-hydroxybenzene)	liq.	203	1·037 at 0°
„	*m*- „ (1- „ 3- „)	— 4	214	1·040 at 0°
„	*p*- „ (1- „ 4- „)	+ 45	219	—
$(CH_3)_3C_6H_2 \cdot OH$	Mesitol (1 : 3 : 5-trimethyl-2-hydroxybenzene)	71	219·5	—
„	Pseudocuminol (1 : 2 : 4-trimethyl-5-hydroxybenzene)	73	235	—
„	Hemimellithenol (1 : 2 : 3- „ 5- „)	81	—	—
$C_3H_7 \cdot C_6H_4 \cdot OH$	*p*-Propylphenol (1-propyl-4-hydroxybenzene)	liq.	232	1·009 at 0°
$(CH_3)_2CH \cdot C_6H_4 \cdot OH$	*p*-Isopropylphenol (1-isopropyl-4-hydroxybenzene)	61	229	—
$(CH_3)_4C_6H \cdot OH$	Prehnitenol (1 : 2 : 3 : 4-tetramethyl-4-hydroxybenzene)	87	266	—
„	Durenol (1 : 2 : 4 : 5-tetramethyl-3-hydroxybenzene)	117	250	—
$(CH_3)_2 : CH \cdot C_6H_3(CH_3) \cdot OH$	Carvacrol (1-methyl-4-isopropyl-2-hydroxybenzene)	0·5	237	0·979 at 20°
„	Thymol (1- „ 4- „ 3- „)	50	232	0·982 at 9·6°
$(CH_3)_3C \cdot C_6H_4 \cdot OH$	*p*-tert. Butylphenol (1-tert. butyl-4-hydroxybenzene)	99	238	0·908 at 114°
$(CH_3)_5C_6 \cdot OH$	Pentamethylphenol (1 : 2 : 3 : 4 : 5-pentamethyl-6-hydroxybenzene)	125	267	—
$(C_2H_5)(CH_3)_2C \cdot C_6H_4 \cdot OH$	tert. Amylphenol (1′ : 1′-dimetho-1-propyl-2-hydroxybenzene)	94	266	—
$(C_2H_5 \cdot CH_2)_2CH \cdot C_6H_4 \cdot OH$	Heptylphenol (1′-propo-1-butyl-4-hydroxybenzene)	71	281	—
$(C_6H_{13})(CH_3)CH \cdot C_6H_4 \cdot OH$	Octylphenol (1′-metho-1-heptyl-4-hydroxybenzene)	liq.	—	—
$C_{16}H_{33} \cdot C_6H_4 \cdot OH$	Hexadecylphenol	77·5	260 (16 mm.)	—
$C_{18}H_{37} \cdot C_6H_4 \cdot OH$	Octadecylphenol	84	277 (15 mm.)	—

carbolic acid (containing 40 per cent. of phenol, the rest creosote, etc.) of sp. gr. 1·05 to 1·06 being thus obtained.[1]

Borck (Ger. Pat. 322,242, 1919) proposes to extract all the phenol from tar-oils by treating them with metallic sodium, $2C_6H_5 \cdot OH + 2Na = 2C_6H_5 \cdot ONa + H_2$; since water is not formed in the reaction, inversion of the latter does not take place as when sodium hydroxide is used.

Phenol is purified by repeated distillation between 175° and 185° or, better, rectification until it crystallises at the ordinary temperature and no longer turns red in the air. To free it from final traces of cresol, it is diluted with 12 to 15 per cent. of water and the hydrate crystallised at −8° to −10° (cresol hydrate crystallises at −20°), centrifuged and distilled until a strength of 99 per cent. is attained; repetition of the operation and of the distillation (in earthenware vessels) gives chemically pure phenol. Minimal quantities of water prevent crystallisation at the ordinary temperature.

Synthetic Preparation of Phenol. This is economically possible when benzene is cheap. Germany supplied Great Britain with synthetic phenol during the Boer War, but after the war the price of phenol became normal again and its manufacture in this way ceased. During the European War (1914 to 1918) enormous quantities of phenol were consumed, not only as an antiseptic, but more particularly for making picric acid to be used as an explosive. Coal-tar phenol being quite insufficient to supply the demand, the manufacture of synthetic phenol from benzene was carried out in various countries on an enormous scale.

Pure benzene is introduced slowly into a steam-jacketed cast-iron boiler containing the necessary amount of concentrated sulphuric acid, the mass being at first mixed without heating and afterwards heated to 115° so as to form benzenemonosulphonic acid. To separate the latter from the excess of sulphuric acid, the acid mixture is poured into a hot, almost saturated sodium sulphate solution, slow cooling then resulting in the separation of a crystalline mass of sodium benzenesulphonate, which is centrifuged and added in small quantities to fused sodium hydroxide, and the temperature finally raised to 320°. The fused mixture of sodium phenoxide and sodium sulphate thus obtained is poured into a small quantity of water, the latter then crystallising out and the phenoxide remaining dissolved. After filtration the solution is treated with sufficient dilute sulphuric acid to liberate the phenol, which floats on the sodium bisulphate solution, and is decanted off and distilled in a vacuum.

Synthetic phenol may be obtained also by heating chlorobenzene with very dilute alkali solution at 300° under pressure (Bergius and Meyer, 1911).

Pure phenol crystallises in colourless needles, melting at 42·5° and boiling unaltered at 181°, but very little water suffices to keep it liquid. It has the sp. gr. 1·084 at 0° and 1·070 at 25°, and it dissolves in 20 parts of water at 16°, in 8 parts at 77°, and in all proportions at 84°; 100 parts of phenol at 9° dissolve 23 parts of water. It is readily soluble in alcohol or ether and has a characteristic odour, this being less marked with synthetic phenol. It is poisonous and 1 grm. on a wound or 8 grm. ingested may cause death; calcium sucrate or sodium sulphite serves as antidote. On account of its great antiseptic power it is largely used as a disinfectant in medicine and surgery[2]; in many cases it is, however, replaced by

[1] **Testing of Carbolic Acid.** Commercial pure phenol melts at 39°, other pure forms melting at 30° to 35° and boiling at 183° to 186°. When pure, phenol should dissolve completely to a clear solution in 15 parts of water and should leave no residue on evaporation. Phenol which does not crystallise at the ordinary temperature contains at least 10 per cent. of higher phenol liquors. The exact quantitative estimation of pure phenol (not containing cresols, which behave like phenol) is effected by transforming it into tribromobenzene by Koppeschaar's method. There is no characteristic reaction for distinguishing the phenols from cresols, but the latter are the less soluble in water. An approximate method, which is used in practice, and is suggested also in the German Pharmacopœia, for determining the phenol-content of crude carbolic acid is as follows: 10 vols. of the product are shaken for a long time with 90 vols. of sodium hydroxide solution (sp. gr. 1·079) in a graduated cylinder and then left to stand until two layers separate; the volume of the undissolved non-phenol is then read off and, after this has been removed, the residue is acidified with HCl and NaCl added to separate the whole of the phenol, the volume of which is subsequently measured.

[2] The action of **Antiseptics or Disinfectants** (*see also* p. 151) depends on the chemical character of the antiseptic substance and partly on the quantity and nature of the substance to be disinfected. The poisonous action of disinfectants is the result of a chemical action with the proteins of the plasma of the living cells, this having varying affinities towards different antiseptics; the concentration of the latter, the duration of the action, etc., also influence the action. With some poisonous and very dilute solutions (the limit of dilution for combination to occur between the proteins and the antiseptic varies with the nature of the latter), certain

other antiseptics (corrosive sublimate, cresols, etc.) which have not the unpleasant odour of phenol. The maximum antiseptic action of phenol is exerted in aqueous solution and in presence of acid, owing to its partial dissociation into the ions $C_6H_5O^1$ and $H^{\cdot}$; according to Pflügge, when dissolved in pure alcohol or in oil, it has no antiseptic action, since it is then not dissociated. It is used for making picric and salicylic acids and dyes.

It dissolves in caustic alkali solutions (forming *phenoxides, e.g.*, $C_6H_5 \cdot ONa$), but not in those of alkali carbonates. With formaldehyde it forms resinous condensation products (Baekelite; *see below*).

A pine splinter, moistened with hydrochloric acid, is coloured bluish green by phenol. As little as 1 part of phenol in 40,000 of water gives a white, flocculent turbidity of tribromophenol on addition of bromine water.

With hydrogen in presence of nickel phenol is converted quantitatively into *cyclohexano* at 160° or into cyclohexanone at 230°. Phenol coagulates proteins.

In 1913 Great Britain exported 8,000 tons of crude phenol (£160,000) and during the European War manufactured and exported enormous amounts of synthetic phenol; in 1919 the exports were only 6500 tons, and in 1920, 9,000 tons.

Before the war the price of commercial dark carbolic acid (25 to 30 per cent.) was about £6 8*s.* to £8 per ton; the 50 to 60 per cent. product, £10 to £12; 100 per cent., £15 to £20; the pale acid, £17 to £28; pure redistilled crystals, m.-pt. 35°, £55; chemically pure crystals, £68; synthetic, £74. *Calcium phenoxide* cost £8 and £14 respectively per ton for the 20 and 50 per cent. products. During the war the prices rose to very high values.

Baekelite, obtained by condensing phenol with formaldehyde, resembles, in appearance and behaviour, certain resins and plastic materials. It was prepared and patented in 1907 by L. H. Baekeland in the United States. Previous experiments in this direction were made by a number of investigators, but Baekeland carried out an exhaustive theoretical and technical examination of the question and found that, according to the temperature conditions and to the nature of the condensing agent employed, three distinct products are obtainable.

1. From phenols and formaldehyde with acid condensing agents, the so-called *sealing wax substitutes*, easily fusible and soluble in alcohol, acetone, alkali, etc., are formed.
2. If the phenol is replaced by a phenolic alcohol, such as saligenin, $OH \cdot C_6H_4 \cdot CH_2 \cdot OH$, and the heating is carried out at 150° in presence of sulphuric acid, a resinous mass, *saliretin*, is formed which is almost insoluble in solvents and softens but does not melt when heated; this represents a polymerised anhydride of saligenin.
3. By condensation of phenols with formaldehyde in presence of alkali (less than one-fifth of that necessary to form the sodium phenoxide) three important products may be obtained; Baekelites A, B and C.

Baekelite A, obtained by protracted heating below 100°, is viscous or liquid in the hot, solid and brittle when cold, and soluble in various solvents; it results from partial anhydridisation of the condensation product of phenols with formaldehyde.

Baekelite B, formed by keeping baekelite A slightly above 100°, is a resinous product insoluble in solvents, but sometimes swelling in them; it softens without melting when heated and may then be moulded. It may be regarded as the complete anhydride of baekelite A.

Baekelite C is obtained by heating baekelite B at 160° to 180°, but in order that the

micro-organisms fix the whole of the metal of the antiseptic (*e.g.*, copper or mercury from their salts); the solution does not then react with hydrogen sulphide, while the cells of the micro-organism do so. The following Table shows the approximate doses of different antiseptics necessary to kill 10 grms. of beer-yeast (containing 30 per cent., *i.e.*, 3 grms., of dry matter), but these numbers would doubtless require considerable modification in the disinfection of other materials:

0·05 to 0·1	grm.	carbolic acid	0·01 to 0·02	grm.	silver nitrate
0·02 ,, 0·04	,,	formaldehyde	0·05 ,, 0·1	,,	zinc sulphate
1·00 ,, 2·00	,,	acetaldehyde	0·05 ,, 0·1	,,	lead acetate
0·5 ,, 0·7	,,	*o*-hydroxybenzaldehyde	0·05 ,, 0·1	,,	hydrochloric acid
0·2 ,, 0·5	,,	acetic acid	0·05 ,, 0·1	,,	caustic soda
0·001 ,, 0·002	,,	copper sulphate	0·02 ,, 0·05	,,	potassium permanganate
0·005 ,, 0·01	,,	corrosive sublimate	0·015 ,, 0·03	,,	chlorine
0·05 ,, 0·1	,,	sodium fluoride	0·5 ,, 1·0	,,	tannin
0·01 ,, 0·025	,,	hydrofluoric acid			

In some cases more concentrated solutions are less active than the more dilute; the activity depends also on the nature of the solvent used.

mass may be free from air and non-spongy, the heating is carried out under pressure of air or CO_2 at 6 to 8 atmos.; superheated steam is used as source of heat.

The mixture used to make baekelite may consist, for example, of 100 parts of phenol, 60 to 120 of concentrated formaldehyde and 4 to 12 of commercial aqueous ammonia. The hot mass becomes first liquid and then viscous, a layer of water separating at the surface and afterwards evaporating; the reaction may be arrested at the A, B or C stage.

Baekelite C has sp. gr. 1·25, is so hard that it cannot be dented by the finger-nail, and is not plastic even when hot; it resists pressure, shock and heat, and does not soften even at 300°; at higher temperatures it chars, burning with difficulty and without flame. It is resistant to the action of moisture, acids and alkalis, but is attacked slightly by hot concentrated sulphuric or nitric acid. It forms an excellent insulator for heat and electricity, and is readily turned or sawn. When pure it is transparent and pale yellow, but during manufacture it may be coloured with alcoholic solutions of aniline dyes. It is almost as elastic as ivory and hence serves for making billiard balls; it also forms a good substitute for amber, celluloid, gallalith (from casein), etc., for making cigar holders, umbrella handles, combs, brushes, tooth-brushes, buttons, gramophone records, etc. The moulds are made of glass, copper or highly polished bronze. Alcoholic solutions of baekelite may be used as varnishes for wood, metal, dynamo coils, paper, etc., the last being rendered hard and dielectric (48,000 volts per mm.). Compressed and baekelised abrasive powders form very hard grindstones.

Various products, similar in character to baekelite, are known. Invelite, patented by Pollak, is obtained from phenol, paraformaldehyde, water and phenolsulphonic acid. Raschig (1912) obtained similar resins by varying the proportions of phenol and formaldehyde and using also cresols, and regards all such products as condensation products of diphenylmethane derivatives. According to Wohl (1913), however, *resite* is a polymerised product of methylene derivatives of the form $CO\left\langle\begin{matrix}CH:CH\\CH:CH\end{matrix}\right\rangle C:CH_2$.

Phenol forms *phenoxides* with many metals (Na, K, Hg, Cu, etc.). The alkali phenoxides, when heated with alkyl iodides, give *ethers*, *e.g.*, **ANISOLE**, $C_6H_5\cdot O\cdot CH_3$(sp. gr. 0·991 at 15°, b.-pt. 132°); **PHENETOLE**, $C_6H_5\cdot O\cdot C_2H_5$ (sp. gr. 0·9822 at 0°, b.-pt. 172°).

These ethers are neutral, very stable liquids, and, as is the case with the corresponding aliphatic compounds, boil at lower temperatures than the phenols.

They are decomposed only in energetic reactions. For instance, hydriodic acid at 140° acts on them with formation of methyl iodide, this reaction serving for the estimation of methoxy-groups in phenolic ethers (Ziesel): $C_6H_5\cdot OCH_3 + HI = CH_3I + C_6H_5\cdot OH$.[1]

[1] *Estimation of Alkoxy-groups by Zeisel's Method.* When the apparatus (Fig. 445) has been found to be air-tight, 0·2 to 0·3 grm. of the substance is introduced into the flask, *A* (30 to 35 c.c.), 50 c.c. of alcoholic silver nitrate (2 grms. fused nitrate + 5 c.c. water + 45 c.c. absolute alcohol)

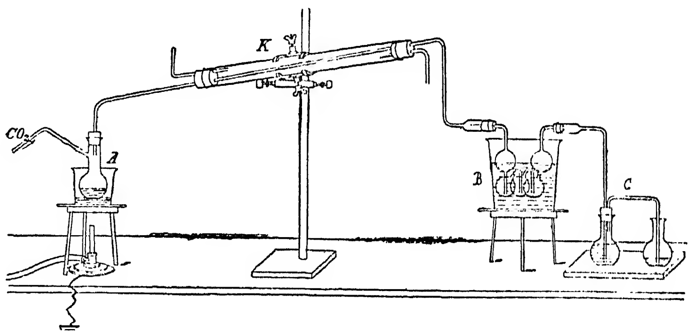


FIG. 445.

into the two flasks, *C*, and then 10 c.c. of pure hydriodic acid (sp. gr. 1·7) into *A*. The latter is then attached to the condenser, *K*, through which water at 40° to 50° circulates; the Geissler bulbs, *B*, which are kept at 50° to 60°, contain water with red phosphorus (0·3 to 0·4 grm.) in suspension to retain hydrogen iodide. The flask, *A*, is heated in a glycerine bath until its contents boil, carbon dioxide being passed slowly (2 bubbles in 2 seconds) through the flask. The operation requires about 15 minutes and is complete when the precipitate formed in *A* separates sharply from the supernatant clear liquid. The total contents of the two flasks, *C*, are diluted in a beaker with 500 c.c. of water and concentrated to about one-half the volume on a water-bath.

Phenol also forms **Acid Derivatives**, *e.g.*, phenylsulphuric acid, $C_6H_5 \cdot O \cdot SO_3H$, which is stable only as salts, these being obtainable, for instance, by the action of aqueous potassium pyrosulphate on potassium phenoxide. They are formed in the urine by the putrefaction of proteins, and are estimated by determining the amount of sulphuric acid liberated in the hot by dilute hydrochloric acid. Carbonic and acetic acids also form analogous compounds.

HALOGEN DERIVATIVES OF PHENOLS. The hydroxyl group of phenol facilitates the replacement of the hydrogen atoms of the benzene nucleus by halogens; even in the cold, bromine water forms **Tribromophenol.** Chlorination can be effected by the direct action of chlorine or by sulphuryl chloride, while replacement by iodine is facilitated in alcoholic solution, or in presence of mercuric oxide (which oxidises the hydriodic acid as it is formed), or in an aqueous alkaline solution. The halogen usually assumes the ortho- or para-position with respect to the hydroxyl.

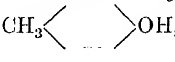
While *o*- or *p*-cresol combines with only two atoms of bromine, the action of chlorine on anisole, $C_6H_5 \cdot O \cdot CH_3$, at 60° in presence of a little iodine, yields *tetra*- or even *pentachloroanisole*, $C_6Cl_5 \cdot OCH_3$. Halogen derivatives of phenols may also be obtained by diazotising halogenated aminophenols.

In general, they are colourless crystalline compounds of pungent odour and decidedly acid character (*trichlorophenol* decomposes carbonates); when they are fused with potash, the halogen atom gives way to another hydroxyl group, which, however, often enters partly in a position different from that occupied by the halogen. Under the further action of chlorine, tri- and penta-chlorophenols yield additive products, the $C \cdot OH$ group being at the same time converted into CO.

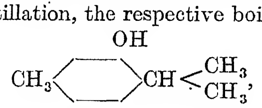
PHENOLSULPHONIC ACIDS, $OH \cdot C_6H_4 \cdot SO_3H$, are obtained by treating phenol with concentrated sulphuric acid, the *o*- and *p*-compounds being formed with equal ease; the *o*- is converted into the *p*-compound by heating with water. The *m*-compound is obtained indirectly by fusing benzene-*m*-disulphonic acid with alkali.

HOMOLOGUES OF PHENOL (*see* Table, p. 639). Oxidation of the side-chains in these leads to aromatic hydroxy-acids.

The **Cresols** are not oxidised by chromic acid mixture, but are completely decomposed by permanganate; if, however, the hydroxylic hydrogen is replaced by an alkyl or by acetyl, oxidation proceeds in the ordinary way.

The three isomeric **Hydroxytoluenes**, $CH_3 \cdot C_6H_4 \cdot OH$, bear the generic name of *cresols.* They are present in wood-tar and in the middle oils of ordinary tar, and may also be prepared from the corresponding amino-derivatives or sulphonic acids. The cresols react with bromine water. The crude cresols mixed with soap solution form *creoline* and *lysol,* which serve as convenient antiseptics and are largely used.[1] ***p*-Cresol,** , is formed in the putrefaction of proteins.

Crude cresols contain the *o*-, *m*- and *p*-isomerides, which cannot be easily separated by fractional distillation, the respective boiling-points being 191°, 203° and 204°.[2]

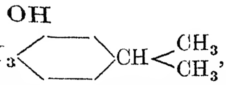
THYMOL, , is found in oil of thyme and has an antiseptic action. One of its iodo-derivatives, **Aristol,** is used as a substitute for iodoform.

A little water and a few drops of nitric acid are then added and the liquid heated until the silver iodide separates, this being then filtered, dried, and weighed in the usual manner. Various modifications of this method have been suggested for volatile substances and especially for those containing sulphur (the substance is hydrolysed with concentrated NaOH and the products absorbed after first passing through a U-tube containing pumice moistened with $CuSO_4$; a current of air and not of CO_2 is used in this case).

[1] **Creoline.** Mixtures of creosote oil and concentrated soap solution were used as disinfectants as early as 1874. Creoline is obtained by protracted heating on a water-bath of a mixture of 1 part of concentrated resin soap solution with 4 parts of medium tar-oils (creosote oils, best with b.-pt. 200° to 210°), the mixture being stirred for several hours and allowed to stand, and the water then separating removed by decantation.

[2] The components may, however, be separated as barium salts. Orthocresol serves for making coumarin perfume and *m*-cresol for making artificial musk, while *p*-cresol is the raw material for preparing anisaldehyde, a delicate perfume sold as *aubepine.*

When a mixture of *p*- and *m*-cresols is treated with sulphuryl chloride, only the *m*-cresol reacts, forming *p-chloro-m-cresol,* which is an excellent *odourless disinfectant,* only slightly soluble in water, but readily emulsified by soap (*see* Creoline); it is sold as *lysochlor.*

CARVACROL, , occurs in *Origanum hirtum*, and is formed by heating camphor with iodine or by the action of phosphoric acid on carvone (*see* Terpenes).

ANETHOLE, $CH_3O \cdot C_6H_4 \cdot CH : CH \cdot CH_3$, is a colourless solid melting at 22°, boiling at 233°, and having the sp. gr. 0·986 at 21·5°; it has a pleasing odour and occurs in *Anise oil* (from the seeds of *Pimpinella anisum*, or the fruits of *Illicium verum* or star-anise), from which it is obtained by repeated fractional distillation or by freezing. Synthetically it is prepared from anisaldehyde and sodium propionate by Perkin's reaction (*see* p. 352), its constitution being thus proved. In the pure state it cost 20*s*. per kilo before the war.

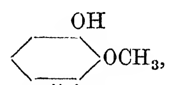
(*b*) DIHYDRIC PHENOLS

These contain two hydroxyl groups united to the carbon of the benzene nucleus. They are analogous in their chemical behaviour to monohydric phenols, and are prepared by similar methods; certain of them show marked reducing properties. With lead acetate, pyrocatechol gives a white precipitate, hydroquinone is precipitated in presence of ammonia, while resorcinol is not precipitated.

PYROCATECHOL (Catechol), $C_6H_4(OH)_2$ (1 : 2), forms crystals melting at 104°, boiling at 240°, and subliming; it dissolves readily in water, alcohol, or ether, and reduces silver salts in the cold and Fehling's solution in the hot. It is found in various resins and is obtained by distilling catechu (*Mimosa catechu*); it is now prepared by fusing *o*-phenolsulphonic acid (*see* p. 643) with caustic potash. It is usually synthesised from *o*-bromo- or *o*-chloro-phenol, which is readily obtained by passing bromine vapour or chlorine into phenol heated at 150° to 170° in a reflux apparatus and purified by washing with alkali and distilling in a vacuum, and is stirred and heated for 8 to 10 hours in an autoclave at 180° to 250° with about its own weight of caustic soda dissolved in one and half times its weight of water. The mass is afterwards dissolved in a little water, acidified with sulphuric acid, and extracted with ether.

It is used as a photographic developer and serves for the preparation of its dimethyl ether, *veratrole*, m.-pt. 22·5°, b.-pt. 205°.

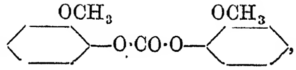
Its alkaline solution is unstable, and is coloured first green and then black by the oxygen of the air; it reduces silver salts, and by ferric chloride is coloured green or violet if a little ammonia is present (*characteristic reaction of ortho-dihydroxy compounds*). With bromine water it gives *tribromoresorcinol*, which melts at 118°, is soluble in water, and turns brown in the air.

Its monomethyl Ether, , is called GUAIACOL and occurs abundantly in beech-tar; it is used in medicine as an expectorant. It is obtained by shaking the creosote oil (fraction boiling at 200° to 250°) from the distillation of the above tar with ammonia, treating with alcoholic potash, washing with ether, crystallising the potassium compound from alcohol, and decomposing it with dilute sulphuric acid. It is obtained crystalline by allowing its light petroleum solution to evaporate slowly. Synthetically it is prepared by diazotising *o*-anisidine, acidifying with dilute sulphuric acid, and distilling in steam.[1] It melts at 29°, boils at 205°, and dissolves in about 60 parts of water at 15°; it is readily soluble in ether or alcohol. With ferric chloride its alcoholic solution gives a blue coloration, changing rapidly to green and then to yellow. It yields *o*-chloroanisole with PCl_5, catechol when fused with alkali, anisole when distilled with zinc dust, and veratrole on methylation; it forms an orange-red picrate, m.-pt. 80°.

Guaiacol is used in the synthesis of vanillin and is employed in medicine as an expectorant and, especially in the form of various salts, in the treatment of pulmonary tuberculosis.[2] Before the war it cost 10*s*. to 13*s*. per kilo.

RESORCINOL, $C_6H_4(OH)_2$ (1 : 3), is formed on fusing various resins, such as *galbanum* and *asafœtida*, with potash, and also from *m*-phenolsulphonic acid or *m*-bromobenzene-

[1] According to Ger. Pat. 305,281 synthetic guaiacol may be obtained by heating catechol at 160° to 180° with alkali salts of methylsulphuric acid in presence of a diluent and slowly adding sodium carbonate or bicarbonate.

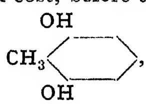
GUAIACOL CARBONATE (*duotal*), , m.pt. 78° to 84°, is odourless

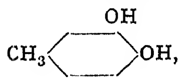
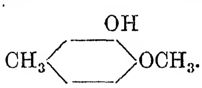
sulphonic acid; it is prepared industrially from *m*- or *p*-benzenedisulphonic acid (prepared from toluene-free benzene) by fusion with potash. It forms rhombic crystals melting at 110°, and boils at 270° with partial decomposition. It turns brown in the air, is soluble in water, alcohol, and ether, and slightly so in benzene, and reduces silver nitrate. It is a less energetic disinfectant than carbolic acid.

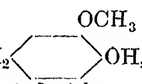
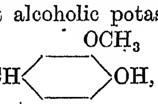
With nitrous acid or diazo-compounds it forms dyes and, like all *m*-dihydroxybenzenes, with phthalic anhydride at 200° it yields fluorescein. Before the war commercial resorcinol cost 4*s*. to 5*s*. per kilo and the pure compound 20*s*. It is largely used in dyeing and printing cotton.

HYDROQUINONE (Quinol), $C_6H_4(OH)_2$ (1 : 4), is obtained by oxidising aniline in the *cold* with sulphuric and chromic acids, or by reducing quinone with sulphurous acid. It forms dimorphous crystals melting at 169°, and with ammonia gives a reddish brown coloration. Oxidising agents convert it into quinone. Owing to its strong reducing properties it is used as a photographic developer.

The chemically pure compound cost, before the war, 8*s*. per kilo.

ORCINOL (Dihydroxytoluene), , does not form fluorescein with phthalic anhydride. Its ammoniacal solution oxidises in the air, giving **Orceine**, $C_{28}H_{24}O_7N_2$, which is the principal component of natural *archil* and is related to litmus.

HOMOPYROCATECHOL (Homocatechol), , gives a monomethyl ether, **Creosol**, .

The unsaturated derivative, **Eugenol**, $CH_2 : CH \cdot CH_2$, is the principal component (90 per cent.) of *clove oil*, from which it is extracted with aqueous potash, being then liberated with acid and rectified in a stream of CO_2. It is a liquid boiling at 247·5° and has the sp. gr. 1·073 at 14°. Hot alcoholic potash displaces the double linking of eugenol, giving **Isoeugenol**, $CH_3 \cdot CH : CH$, which also has a pleasant, characteristic odour.

(*c*) TRIHYDRIC PHENOLS (Trihydroxybenzenes)

The constitutions of the three isomeric trihydroxybenzenes have now been fixed with certainty: **Pyrogallol**, 1 : 2 : 3; **Hydroxyhydroquinone**, 1 : 2 : 4 : (*as*), and **Phloroglucinol**, 1 : 3 : 5 (*s*).

PYROGALLOL (1 : 2 : 3-**Trihydroxybenzene**; also improperly called **Pyrogallic acid**), $C_6H_3(OH)_3$, is prepared by heating gallic acid (*see later*) for half an hour in an autoclave at 200° to 210° with 2 to 3 times its weight of water; the solution is decolorised by boiling with animal charcoal, filtered, concentrated, and crystallised. The pyrogallol thus obtained is purified by sublimation and then forms shining, white, poisonous scales or needles, melting at 132° and boiling at 210°. It may also be prepared by distilling a mixture of 1 part of gallic acid with 2 parts of powdered pumice in a current of CO_2.

It dissolves in 1·7 part of water or ether, or in 1 part of alcohol. In alkaline solution it is an energetic reducing agent and absorbs oxygen from the air with avidity; it is used in gas analysis in all cases in which oxygen is to be absorbed (see Orsat Apparatus, Vol. I., p. 463). By fresh solutions of ferrous sulphate it is coloured blue, by ferric chloride brown, and by silver nitrate black.

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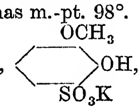
and almost tasteless, insoluble in water and soluble in hot alcohol.

Guaiacol phosphate, $PO(O \cdot C_6H_4 \cdot OCH_3)_3$, has m.-pt. 98°.

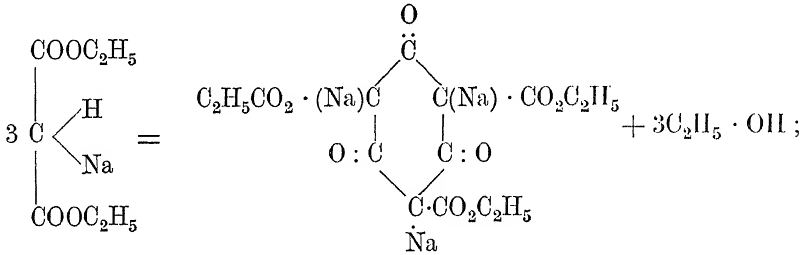
Potassium guaiacol-o-sulphonate (*thyocoll*), , is soluble in water and slightly so in alcohol.

It does not react with hydroxylamine (*see* Phloroglucinol). Its dimethyl ether (**Dimethyl pyrogallate**), $OH \cdot C_6H_3(OCH_3)_2$, is contained, along with other homologous ethers, in beech-tar.

It is used in photography, in electro-plating, in medicine, and in hair dyes. When pure it cost, before the war, 12*s*. to 14*s*. 6*d*. per kilo.

HYDROXYHYDROQUINONE (**1 : 3 : 4-Trihydroxybenzene**), $C_6H_3(OH)_3$, is obtained by fusing hydroquinone with caustic soda and has not been very closely studied. It crystallises from ether in plates melting at 140·5°, readily undergoes change in aqueous solution, and does not react with hydroxylamine (*see* Phloroglucinol).

PHLOROGLUCINOL, $C_6H_6O_3$, is obtained by fusing various resins with KOH. Baeyer prepared it synthetically by condensing 3 mols. of ethyl sodiomalonate in the hot, 3 mols. of alcohol being thus eliminated :



acidification of this product results in the substitution of the sodium by hydrogen with formation of *phloroglucinoltricarboxylic acid*, which, when fused with caustic potash, loses its carbethoxy-groups and gives phloroglucinol. The latter should, therefore, have the constitution $CO{<}{\genfrac{}{}{0pt}{}{CH_2-CO}{CH_2-CO}}{>}CH_2$ which contains no double linking and corresponds with *triketohexamethylene ;* in accord with this structure, it reacts with 3 mols. of hydroxylamine, giving a trioxime.

On the other hand, it behaves also as a trihydroxybenzene or trihydric phenol, giving a triacetyl-derivative with acetyl chloride, so that it is able to exist in two tautomeric forms.

This explains why, when it is treated with alcoholic potash or with an alkyl iodide, the alkyl groups unite with carbon and not with oxygen (as they would with a triphenol), giving, *e.g.*, hexamethylphloroglucinol.

Pure phloroglucinol cost, before the war, about £16 per kilo.

(*d*) POLYHYDRIC PHENOLS

From dinitroresorcinol is obtained a **Tetrahydroxybenzene**, $C_6H_2(OH)_4$ (1 : 2 : 4 : 5), which boils at 220°, while chloranilic acid (*see later*) is formed by the oxidation of the dichloro-derivative.

HEXAHYDROXYBENZENE, $C_6(OH)_6$, is obtained as potassium derivative, $C_6O_6K_6$, in the manufacture of potassium by reduction of its carbonate : $K_2CO_3 + C_2 = 3CO + K_2$ and $6K + 6CO = C_6O_6K_6$. These reactions represent a further example of the synthesis of organic substances from inorganic matter. Hexahydroxybenzene is a white, crystalline substance which oxidises readily in the air and yields benzene when distilled with zinc dust.

Of the additive products formed by polyhydric phenols with hydrogen, *quercitol* and *inositol* may be mentioned.

QUERCITOL (**Pentahydroxycyclohexane or Acorn Sugar**)

$$OH \cdot CH{<}{\genfrac{}{}{0pt}{}{CH(OH) \cdot CH(OH)}{CH(OH) \cdot CH(OH)}}{>}CH_2,$$

is found in acorns and is similar to mannitol ; it has a sweet taste and forms monoclinic prisms melting at 234°, its specific rotation being $[\alpha]_D^{16} = + 24 \cdot 16°$. When heated to 240°

in a vacuum or fused with alkali it loses water yielding various aromatic derivatives (hydroquinone, quinone, and pyrogallol); on reduction with HI, it gives benzene, phenol, pyrogallol, quinone, and hexane. When oxidised with nitric acid it forms mucic and trihydroxyglutaric acids, while with permanganate it yields malonic acid, the presence of the methylene group, CH_2, being thus confirmed. It forms a pentacetyl-derivative, an explosive pentanitrate, and a pentachlorohydrin, $C_6H_7Cl_5$, melting at 102°; the formation of these compounds demonstrates the presence of five hydroxyl groups.

INOSITOL (Hexahydroxycyclohexane or Muscle Sugar), $C_6H_6(OH)_6$, is similar to quercitol, but contains a $CH \cdot OH$ group in place of the CH_2. It has the appearance and, to some extent, the sweet taste of the sugars, with which it was for long confused. That it is a cyclohexane derivative is shown by the formation of phenol, benzene, and tri-iodophenol on reduction with HI, and that of quinone and some of its derivatives on treatment with PCl_5. The presence of six hydroxyl groups is proved by the formation of a *hexa-acetate* (m.-pt. 212°) when it is treated with acetic anhydride and zinc chloride, and of a *hexanitrate*, $C_6H_6(NO_3)_6$ (m.-pt. 120°), under the action of concentrated sulphuric and nitric acids; the hexanitrate is highly explosive and reduces Fehling's solution. Four optical isomerides are known: (1) inactive; (2) dextro-rotatory, $[\alpha]_D + 68{\cdot}4°$, crystallising with $2H_2O$ and melting at 247°; (3) lævo-rotatory, $[\alpha]_D - 65°$, m.-pt. 247°; (4) racemic, melting at 250°. Baeyer's stereochemical conceptions indicate eight possible isomerides, according to the arrangement of the OH and H above or below the plane of the hexagon. Inositol, especially the inactive form, occurs in beans, lentils, peas, the muscles of the heart, the brain, etc. The inactive modification crystallises from water with $2H_2O$ at temperatures below 50°, and in an anhydrous form, m.-pt. 225°, at higher temperatures; it boils unchanged in a vacuum at 319° and is not fermented by yeasts. It does not combine with phenylhydrazine or reduce Fehling's solution, but it reduces ammoniacal silver nitrate solution; it forms a basic lead salt, $(C_6H_{11}O_6)_2Pb, PbO$. It does not yield quercitol when reduced, so that the hydroxyl groups are symmetrically distributed.

The monomethyl ether of *i*-inositol, or *bornesitol*, is found in Borneo rubber, and the dimethyl ether, or *dambonitol*, $C_6H_6(OH)_4(OCH_3)_2$, in Gabon rubber. The monomethyl ether of *d*-inositol, or *pinitol*, which occurs in many plants and plant-juices, melts at 186°, sublimes at 200°, and has a rotation of + 67·5°. The monomethyl ether of *l*-inositol, or *quebrachitol*, melts at 186°, boils at 200° *in vacuo*, and with HI forms *l*-inositol; it occurs in quebracho bark.

E. QUINONES

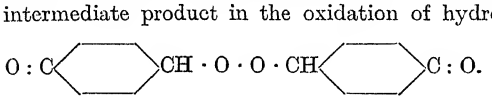
These may be regarded as derivatives of phenols obtained by elimination of hydroxyl groups, with consequent displacement and partial elimination of the double linkings of the benzene nucleus. They are usually yellow and of pungent odour and possess oxidising properties; they are volatile in steam, with partial decomposition.

Oxidation of meta- and ortho-diphenols does not yield quinones.

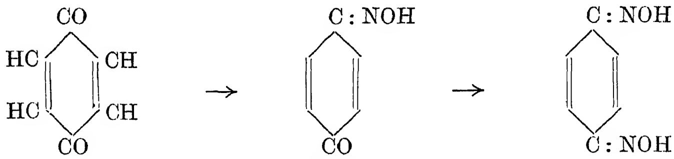
BENZOQUINONE or simply Quinone, $C_6H_4O_2$, can be obtained by oxidising either *p*-aminophenolor sulphanilic acid ($1:4 - NH_2 \cdot C_6H_4 \cdot SO_3H$), or *p*-phenolsulphonic acid, or hydroquinone, or aniline (on a large scale) with chromic acid.

On sublimation it forms fine yellow crystals which melt at 116°, giving a characteristic odour. It is soluble in alcohol or ether and slightly so in cold water. It fixes hydrogen, which transforms it into hydroquinone, while the halogens give addition or substitution products according to the conditions. With HCl it forms monochlorohydroquinone, $C_6H_4O_2 + HCl = C_6H_3Cl(OH)_2$. With amines and with phenols it forms dyes which crystallise well but are only slightly soluble.

With hydroquinone it forms a condensation product, Quinhydrone, $C_6H_4O_2 \cdot C_6H_4(OH)_2$, which consists of green prisms with a metallic lustre, and may be regarded as an intermediate product in the oxidation of hydroquinone or in the reduction of quinone,

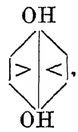
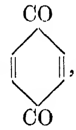


Constitution. That *quinone* contains two carbonyl groups is deduced from the fact that with hydroxylamine it yields *quinonemonoxime* and *quinonedioxime :*



Qninonemonoxime
(nitrosophenol)

It contains two double linkages, since in benzene solution it absorbs four atoms of bromine, while ozone is also fixed quantitatively (*see* pp. 107 and 359).

The transformation of hydroquinone, , into quinone, , is an evident example of the convertibility of the centric form of benzene into that with two double linkages.

Tetrachloroquinone (*chloranil*), $C_6Cl_4O_2$, prepared by oxidising trichlorophenol with dichromate and sulphuric acid, serves for the manufacture of coal-tar dyes. *Toluquinone*, $C_6H_3O_2 \cdot CH_3$, *xyloquinone*, *thymoquinone*, etc., are known, as also are *quinoneimides* (*e.g.*, $C_6H_4O \cdot NH$) and *quinonediimides* [*e.g.*, $C_6H_4(NH)_2$].

F. NITRO-DERIVATIVES OF AROMATIC HYDROCARBONS

These are readily obtained by treating the hydrocarbons with concentrated nitric acid, best in presence of concentrated sulphuric acid, which fixes the water as it is formed :

$$C_6H_6 + HNO_3 = H_2O + C_6H_5 \cdot NO_2.$$

With the hydrocarbons homologous with benzene, nitration is still more easy, but not more than three nitro-groups can be introduced directly; tetranitro-derivatives are prepared indirectly. Aromatic nitro-compounds cannot be obtained by the action of silver nitrite on chlorobenzenes, as is the case with those of the fatty series, but this method serves for the introduction of nitro-groups into side-chains.

The nitro-compounds are liquid or solid and usually more or less yellow, although some are red ; they are heavier than water and dissolve readily in alcohol, ether, or acetic acid, but are mostly insoluble in water. They distil unchanged and are volatile in steam.

The nitro-group is united very firmly to the nucleus, especially in mononitrobenzene, and is not directly replaceable. It can be reduced to the *amino-group* by means of nascent hydrogen in *acid* solution[1] ; reduction in alkaline solution results in the formation of azoxy-, azo-, and *hydrazo-compounds*, whilst in neutral solution or with hydrogen sulphide, the nitro-group becomes a hydroxylamino-group. On electrolytic reduction, nitro-derivatives yield amino-phenols.

Polynitrobenzenes are easily obtained by the action of fuming nitric acid in the hot ; the meta-derivative is formed first, and this, by further nitration with nitric and fuming sulphuric acids at 140°, gives symm. trinitrobenzene.

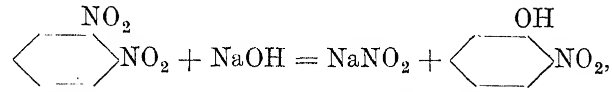
The polynitro-compounds react more readily than mononitro-derivatives ; when the former are oxidised, a phenolic group is formed, while the nitro-groups remain intact.

With para- and ortho-dinitrobenzenes, sodium alkoxide replaces one nitro-group quantitatively, whilst with *m*-dinitrobenzene no reaction occurs :

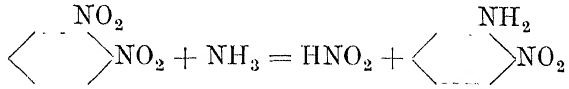
$$C_6H_4(NO_2)_2 + C_2H_5 \cdot ONa = NaNO_2 + NO_2 \cdot C_6H_4 \cdot OC_2H_5.$$

[1] The nitrogen of aromatic derivatives in which the nitro-group is united directly to the benzene nucleus may be determined by the Kjeldahl method only when this is suitably modified.

By boiling *o*-dinitrobenzene with caustic soda, *o*-nitrophenol is formed :



while boiling with alcoholic ammonia yields *o*-nitraniline :



NITROBENZENE, $C_6H_5 \cdot NO_2$, is an almost colourless, faintly yellow, refractive liquid which has the sp. gr. 1·209 at 15° and, after solidification, melts at 3° and boils at 206°. Owing to its pleasant bitter-almond smell, it is used in perfumery under the name of artificial *essence of mirbane*, but its vapour is somewhat poisonous. It is insoluble in water, but it mixes in all proportions with alcohol, ether, or benzene.

It is of considerable industrial importance, as it forms the raw material for the manufacture of aniline, benzidine, quinoline, azobenzene, various explosives, etc.

On a large scale it is prepared in wrought- or cast-iron vessels, employing precautions and methods similar to those used in making nitroglycerine (*see* p. 278). The nitro-sulphuric mixture, consisting of 120 kilos of HNO_3 (42° Bé). and 180 kilos of H_2SO_4 (66°Bé.), is poured gradually (in 8 hours) into 100 kilos of benzene. The mass is kept mixed by means of a stirrer, and during the first 5 to 6 hours is maintained at 25° by means of cold water circulating outside the apparatus. In the final phase of the reaction the temperature is raised by external steam to 70° to 90°, the heating being then stopped, while the stirring is continued for a further 6 hours. The mass is then forced by a suitable elevator into a tank with a conical base. The acid mixture gradually settles to the bottom, while the nitrobenzene floats ; the former is then drawn off through taps (*see* Nitroglycerine), and the nitrobenzene, after repeated washing with water, distilled in a current of steam from a vessel with a jacketed bottom heated with steam at 2 to 3 atmos. pressure. A second distillation yields moderately pure nitrobenzene. According to Ger. Pat. 221,787 of 1907, nitrobenzene can also be obtained by running benzene into a mixture of sulphuric acid and sodium nitrate at 70° to 90°. It was sold at £36 to £52 per ton before the war.

DINITROBENZENES. By the action of fuming nitric acid or of a suitable nitro-sulphuric mixture on benzene, *m*-dinitrobenzene is formed along with small proportions of the ortho- and para-compounds. The meta-derivative crystallises from alcohol in pale yellow rhombic plates, m.-pt. 90°, b.-pt. 297°, and is insoluble in water, but readily soluble in alcohol or ether.

Its heat of combustion is 4103 cals. per grm. When boiled with sodium hydroxide it is converted into *m-dinitroazoxybenzene*, $NO_2 \cdot C_6H_4 \cdot NO : N \cdot C_6H_4 \cdot NO_2$. It is often mixed with other explosives, *e.g.*, trinitrotoluene, to lower the melting-point. It is used on a large scale, not only for explosives, but for making dyes and *m*-phenylenediamine and *m*-nitraniline.

The ortho- and para-isomerides, melting at 117° and 172° respectively, are not of industrial importance, and are obtained either from the mother liquors of the meta-compound or, indirectly, from the corresponding dinitroanilines.

TRINITROBENZENES, $C_6H_3(NO_2)_3$. The three possible isomerides are known. The symmetrical, 1 : 3 : 5-compound, is obtained by protracted heating of *m*-dinitrobenzene with a concentrated mixture of nitric and sulphuric acids. The asymmetric, 1 : 2 : 4-compound, m.-pt. 62°, is formed similarly from *p*-dinitrobenzene. The vicinal, 1 : 2 : 3-compound, m.-pt. 127·5°, was obtained by Körner and Contardi only in 1914 by diazotising 2 : 6-dinitroaniline.

s-**Trinitrobenzene**, m.-pt. 121° to 122°, dissolves sparingly in water, to a somewhat greater extent in methyl or ethyl alcohol, and readily in acetone, ether or benzene. Its explosive properties are superior to those of trinitrotoluene or picric acid, the equation

More Important Nitro-Derivatives

Formula	Name	Positions of groups		Melting-point	Boiling-point	Specific gravity
		Alkyl	Nitro			
$C_6H_5 \cdot NO_2$	Nitrobenzene	—	1	+ 3°	208°	1·204 at 20°
$C_6H_4(NO_2)_2$	*o*-Dinitrobenzene	—	1 : 2	117°	319°	—
,,	*m*- ,,	—	1 : 3	90°	302°	1·369 at 98°
,,	*p*- ,,	—	1 : 4	172°	299°	—
$C_6H_3(NO_2)_3$	sym. Trinitrobenzene	—	1 : 3 : 5	122°	—	—
,,	as. ,,	—	1 : 2 : 4	57·5°	—	—
$C_6H_4(CH_3)(NO_2)$	*o*-Nitrotoluene (methylnitrobenzene)	1	2	− 10·5°	218°	1·168 at 15°
,,	*m*- ,, ,,	1	3	+ 16°	230°	1·168 at 22°
,,	*p*- ,, ,,	1	4	54°	236°	1·123 at 54°
$C_6H_3(CH_3)(NO_2)_2$	Dinitrotoluene (methyldinitrobenzene)	1	2 : 4	70°	—	1·321 at 70°
$C_6H_3(CH_3)_2(NO_2)$	Nitro-*o*-xylene (dimethylnitrobenzene)	1 : 2	4	29°	258°	1·139 at 30°
,,	,, -*m*- ,, ,,	1 : 3	4	2°	246°	1·135 at 15°
,,	,, -*p*- ,, ,,	1 : 4	2	liquid	240°	1·132 at 15°
$C_6H_2(CH_3)_2(NO_2)_2$	Dinitro-*m*-xylene (dimethyldinitrobenzene)	1 : 3	2 : 4	82°	—	—
,,	,, -*m*- ,, ,,	1 : 3	4 : 6	93°	—	—
$C_6H(CH_3)_2(NO_2)_3$	Trinitro-*m*-xylene (dimethyltrinitrobenzene)	1 : 3	2 : 4 : 6	182°	—	—
$C_6H_2(CH_3)_3(NO_2)$	Nitromesitylene (trimethylnitrobenzene)	1 : 3 : 5	2	44°	255°	—
$C_6H(CH_3)_3(NO_2)_2$	Dinitromesitylene (trimethyldinitrobenzene)	1 : 3 : 5	2 : 4	86°	—	—
$C_6(CH_3)_3(NO_2)_3$	Trinitrohemimellithene (trimethyltrinitrobenzene)	1 : 2 : 3	4 : 5 : 6	209°	—	—
,,	Trinitropseudocumene ,,	1 : 2 : 4	3 : 5 : 6	185°	—	—
,,	Trinitromesitylene ,,	1 : 3 : 5	2 : 4 : 6	231°	—	—
$C_6H(CH_3)_4(NO_2)$	Nitroprehnitene (tetramethylnitrobenzene)	1 : 2 : 3 : 4	5	61°	295°	—
$C_6H_3(CH_3)(C_3H_7)(NO_2)$	Nitrocymene (methylisopropylnitrobenzene)	1 : 4	2	liquid	—	1·085 at 15°
$C_6(CH_3)_4(NO_2)_2$	Dinitroprehnitene (tetramethyldinitrobenzene)	1 : 2 : 3 : 4	5 : 6	178°	—	—
,,	Dinitroisodurene ,,	1 : 2 : 3 : 5	4 : 6	156°	—	—
,,	Dinitrodurene ,,	1 : 2 : 4 : 5	3 : 6	205°	—	—
$C_6H(CH_3)(C_4H_9)(NO_2)_3$	Trinitro-tert. butyltoluene	1 : 3	2 : 4 : 6	97°	—	—

representing the theoretical decomposition being $2C_6H_3(NO_2)_3 = 9CO + 3H_2O + 3N_2 + 3C$. It readily forms additive compounds with organic bases and hydrocarbons.

With a view to the use of this compound as an explosive, attempts have been made, but with unsatisfactory results, to prepare it either by nitrating dinitrobenzene, or dehalogenating chlorodinitrobenzene by means of reduced copper, or by oxidising trinitrotoluene (*see later*) with sulphuric and chromic acids (Ger. Pat. 127,325) and decomposing the resultant trinitrobenzoic acid by heat.

NITROTOLUENES

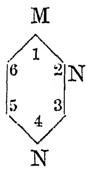
Nitration of toluene by nitric acid either alone or mixed with sulphuric acid, under conditions yielding mononitrotoluenes, gives always a mixture containing about 57, 40 and 3 per cent. of the *o*-, *p*- and *m*- compounds respectively. Further nitration of *m*-nitrotoluene yields the 2 : 3-, 3 : 4- and 3 : 6-dinitro-compounds; the 3 : 5-compound, when obtained otherwise, does not give trinitrotoluenes when further nitrated.

Direct nitration of toluene or mono- or di-nitrotoluenes yields only 2 : 4 : 6- (α), 2 : 3 : 4- (β), and 2 : 4 : 5- (γ)-trinitrotoluenes, but the other three isomerides, 3 : 4 : 5- (δ), 2 : 3 : 5- (ϵ) and 2 : 3 : 6- (η), have been recently prepared indirectly by Körner and Contardi (1914–1917). Tetra- and penta-nitrotoluenes are unknown.

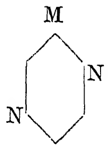
MONONITROTOLUENES. The three isomerides may be separated to some extent by fractional distillation and crystallisation.

o-**Nitrotoluene** is obtained pure by reducing 2 : 4-dinitrotoluene by means of ammonium sulphide, diazotising the 2-nitro-4-toluidine formed and decomposing the diazo-compound with boiling alcohol. It exists in two morphotropic forms, solidifying at − 10° and − 4°, and is used for making *o*-nitrochlorobenzil, *o*-nitrobenzaldehyde, *o*-hydrazotoluene and *o*-toluidine. *m-Nitrotoluene* is obtained similarly from the diazo-compound derived from 3-nitro-4-toluidine, and occurs in the liquid portion of the dinitrotoluene prepared industrially in the manufacture of trinitrotoluene; it has few practical applications. *p-Nitrotoluene* serves for making *p*-nitro- and *p*-amino-benzaldehyde and, especially, *p*-nitrotoluene-*o*-sulphonic acid, which is used in the manufacture of amine A fast yellow and Mikado orange 4R. With alcoholic sodium hydroxide it gives an orange coloration of dinitroazostilbene (Green) or dinitroazoxystilbene (Giua).

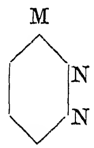
DINITROTOLUENES, $C_6H_3(CH_3)(NO_2)_2$, exist in six isomeric forms, which are prepared and named in various ways. Denoting the methyl group by M (always in position 1) and the nitro-group by N, the isomerides have the following configurations:



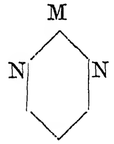
m-dinitrotoluene
ordinary dinitrotoluene
o : *p*-dinitrotoluene
α-dinitrotoluene
2 : 4-dinitrotoluene
m.-pt. 70·5°



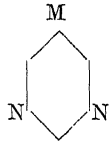
p-dinitrotoluene
ϵ-*p*-dinitrotoluene
2 : 5-dinitrotoluene
m.-pt. 52·5°



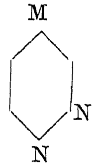
o : *m*: dinitrotoluene
1 : 2 : 3-dinitrotoluene
m.-pt. 63°



o : *o*-dinitrotoluene
β-dinitrotoluene
2 : 6-dinitrotoluene
m.-pt. 65·5°



m : *m*-dinitrotoluene
δ-dinitrotoluene
3 : 5-dinitrotoluene
m.-pt. 92°



m : *p*-dinitrotoluene
γ-dinitrotoluene
3 : 4-dinitrotoluene
m.-pt. 60°

Of the various names, the last given in each case is the simplest and clearest.

2 : 4-**Dinitrotoluene** is prepared similarly to nitrobenzene and is the one in most common industrial use, while it serves also for making ordinary (2 : 4 : 6) trinitrotoluene. It is purified by crystallisation from alcohol or carbon disulphide and forms monoclinic crystals melting at 70·5°; it is insoluble in water, slightly soluble in cold alcohol or ether, still less

so in carbon disulphide (2·2 per cent.), and readily soluble in benzene. It dissolves in alkali, giving a red solution, from which acids precipitate a reddish brown substance. In acetone solution it is coloured blue by caustic potash. It decomposes at 300°, but distils unchanged in a vacuum. Fuming nitric acid oxidises it slowly, and in the hot gives the corresponding *o* : *p-dinitrobenzoic acid*, $C_6H_3(CO_2H)(NO_2)_2$. With hot, concentrated nitro-sulphuric mixture, it forms ordinary trinitrotoluene (*see below*). Ammonium sulphide reduces it in the cold to *o-nitro-p-toluidine* (m.-pt. 105°), while in the hot, *p-nitro-o-toluidine* (m.-pt. 78°) is also formed. By zinc and hydrochloric acid it is reduced to *tolylenediamine*.

2 : 6-Dinitrotoluene is obtained along with the 2 : 4-isomeride and accumulates in the mother-liquors, when mononitrotoluene (ortho) is nitrated further. It is prepared in the pure state by eliminating the amino-group from dinitro-*p*-toluidine (m.-pt. 168°). It forms shining needles, m.-pt. 65·5°, dissolves to some extent in alcohol, and with ammonium sulphide gives *o*-nitro-*o*-toluidine. With acetone and alkali it gives no coloration.

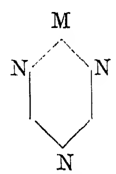
2 : 3-Dinitrotoluene is obtained by heating *o* : *m*-dinitro-*p*-toluic acid with dilute hydrochloric acid for 6 hours at 265° and distilling in a current of steam, the crystals formed being pressed or centrifuged ; it separates from light petroleum solution in yellow crystals, m.-pt. 63°.

2 : 5-Dinitrotoluene is obtained together with the 2 : 4-derivative when toluene or nitrotoluene is run into fuming nitric acid ; it crystallises from alcohol in yellow needles, m.-pt. 52·5°. Alcoholic ammonium sulphide reduces it to *o*-nitro-*m*-toluidine.

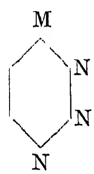
3 : 5-Dinitrotoluene is formed by eliminating the amino-group by diazotisation (*see* Aniline) from dinitro-*o*-toluidine (m.-pt. 208°) or from *m* : *m*-dinitro-*p*-toluidine (m.-pt. 168°). From water, in which it is sparingly soluble, it crystallises in needles, m.-pt. 92°. It is soluble slightly in light petroleum, more so in cold alcohol or in carbon disulphide, and readily in chloroform, ether, or benzene. It distils easily in a current of steam, and with benzene forms the crystalline double compound, $C_6H_3(CH_3)(NO_2)_2 + C_6H_6$.

3 : 4-Dinitrotoluene is obtained by protracted agitation of *m*-nitrotoluene with concentrated nitric acid (sp. gr. 1·54). From carbon disulphide (which dissolves 2·19 per cent.), it crystallises in long needles melting at 60°.

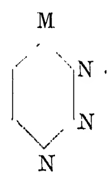
TRINITROTOLUENES. The following six isomerides are possible, all being known :



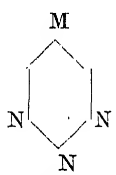
α-(2 : 4 : 6-)trinitrotoluene melts at 80.-6°



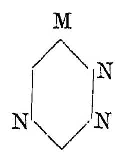
β-(2 : 3 : 4-)trinitrotoluene m.-pt. 112°



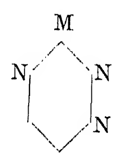
γ-(2 : 4 : 5-)trinitrotoluene m.-pt. 104°



δ-(3 : 4 : 5-)trinitrotoluene m.-pt. 137·5°



2 : 3 : 5-trinitrotoluene m.-pt. 97·2°



η-(2 : 3 : 6-)trinitrotoluene m.-pt. 111°

α-TRINITROTOLUENE (*ordinary* or **2 : 4 : 6-Trinitrotoluene**) forms long, pale yellow, prismatic crystals, m.-pt. 80·65° (corrected), deflagrating above 260° but distilling unchanged in a vacuum. A pressure of 2500 atmos. increases the density of the crystalline mass to 1·59, whereas a pressure of 3 to 4 atmos. on the material during crystallisation, combined with shaking, gives a density of 1·61.

This compound is slightly soluble in water or light petroleum, more so in alcohol or carbon disulphide, and readily so in acetone, ether, benzene, toluene or chloroform. The action of sunlight and air turns it brown and lowers its melting-point. By concentrated nitric acid at 110°, or concentrated sulphuric acid and chromic acid at 50° to 60°, it is turned into *s*-trinitrobenzoic acid, whilst fuming nitric acid at 200° converts it into trinitrobenzene.

With caustic alkali, alkali carbonate or potassium cyanide it gives a deep reddish-brown or violet coloration.

With various organic bases it forms red additive compounds.

When aniline is poured into an alcoholic solution of trinitrotoluene, a double compound $C_6H_2(CH_3)(NO_2)_3 + C_6H_5 \cdot NH_2$, separates in red acicular crystals melting at 84°. Whilst picric acid readily forms with metals picrates dangerous to handle, trinitrotoluene (*see* p. 304) does not react with metals and can be manipulated safely even in the hot, since it burns slowly without exploding; it is not hygroscopic and does not form a bitter and poisonous dust like picric acid. It is highly stable to shock, and when compressed is exploded with a mercury fulminate cap, but when fused and then solidified it is exploded only by a detonator of moderately compressed, crystalline trinitrotoluene, which in its turn is exploded by a fulminate cap. The *velocity of detonation* in a charge 50 mm. in diameter and with a density of 1·55 is 7500 metres (picric acid, 8000 metres) per sec.

The theoretical decomposition is expressed by: $2C_6H_2(CH_3)(NO_2)_3 = 12CO + 2CH_4 + H_2 + 3N_2$, 1 kilo giving 778 litres of gases, which are incompletely burnt owing to lack of oxygen. If the gases formed are free from methane (*see* Note, p. 259), the equation would be rather, $2C_7H_6(NO_2)_3 = 12CO + 6H_2 + 3N_2 + 2C$.

The use of trinitrotoluene as an explosive was suggested in 1891, and attempts were made to compensate the deficiency of oxygen by addition of ammonium nitrate, but it has been largely used, mainly as a result of Bichel's investigations, only since 1904, and in the crystalline state it now forms a very important military explosive. In the compressed or solidified state it is used for charging projectiles, grenades, etc. (it does not serve for propelling projectiles, owing to its shattering power and to the abundance of fumes it forms on explosion). Different firms produce it under various names (*trotyl, trolite, trilite, trinol, tritole*).

Industrially it is made by nitration of mono- or di-nitrotoluene, and its purity is checked by determination of its melting-point. During the European War it was manufactured in enormous quantities in the various combatant countries.

For some time a plastic product called *plastrotyl* (Bichel, 1906) was prepared from trinitrotoluene, resin, collodion-cotton, and crude liquid dinitrotoluene, but this is no longer manufactured.

β-TRINITROTOLUENE or **2 : 3 : 4-Trinitrotoluene** is formed in small proportion with a large proportion of the γ-isomeride (*see below*) when *m*-nitrotoluene is boiled for a day with nitric and sulphuric acids, and may be obtained also by nitrating 2 : 3- or 3 : 4-dinitrotoluene. With hot alcoholic ammonia it gives *β-dinitrotoluidine,* m.-pt. 94°.

γ-TRINITROTOLUENE or **2 : 4 : 5-Trinitrotoluene** is formed with the β-isomeride (*see above*), from which it can be separated in virtue of its slight solubility in alcohol or carbon disulphide. It forms yellowish, shining crystals, melting at 104°. Its physical and chemical properties are similar to those of its isomerides.

The δ-, ϵ- and η-compounds also exhibit similar properties.

***o*-NITROCHLOROBENZENE** (m.-pt. 32·5°, b.-pt. 246°) and ***p*-NITROCHLOROBENZENE** (m.-pt. 83°, b.-pt. 239°), are obtained together by nitration of chlorobenzene. The chlorine atom in these compounds is very mobile and is readily replaced by OH, OCH_3, NH_2 or NHC_6H_5. The meta-isomeride, m.-pt. 44·4°, b.-pt. 235·6°, is of less importance. All are very poisonous.

2 : 4-DINITROCHLOROBENZENE is an important product, being used in making dinitrophenol, and hence Sulphur Black T, dinitroaniline, picric acid, nitroaminophenol, and di-, tetra, and hexa-nitrodiphenylamines. It may be obtained in almost theoretical yield by suitable nitration of chlorobenzene.

It forms rhombic crystals, sp. gr. 1·697, m.-pt. 51°, b.-pt. 315° (slight decomposition), and is a poisonous product with an irritating action on the skin, this being apparently due to the presence of the 2 : 6-isomeride.

TRINITROtert. BUTYLXYLENE has an odour of musk and is used as a perfume.

PHENYLNITROMETHANE, $C_6H_5 \cdot CH_2 \cdot NO_2$, contains the nitro-group in the side-chain, as is shown by its method of preparation:

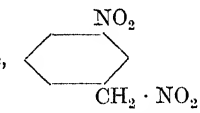
$$\underset{\text{Benzyl chloride}}{C_6H_5 \cdot CH_2Cl} + AgNO_2 = AgCl + C_6H_5 \cdot CH_2 \cdot NO_2.$$

It is obtained also by heating toluene with nitric acid (sp. gr. 1·12) under pressure. This compound exists in two isomeric (or tautomeric) forms, one being known as a *pseudo-*

acid: (1) $C_6H_5 \cdot CH_2 \cdot NO_2$ and (2) $C_6H_5 \cdot CH : NO \cdot OH$ (pseudo-acid); the former does not react with ferric chloride, while the latter gives a coloration. Modification (1) is a liquid, and its aqueous solution gives, with sodium alkoxide, the sodium salt of the pseudo-acid; when the acid is liberated by means of a mineral acid it forms a crystalline product, which has the same composition as the original compound and gradually changes into this, becoming liquid. The presence of a hydroxyl group in the pseudo-acid is demonstrated by the formation of the characteristic *dibenzhydroxamic* (or dibenzoylhydroxamic) acid by treatment with benzoyl chloride:

$$C_6H_5 \cdot CH : NO \cdot ONa + C_6H_5 \cdot CO \cdot Cl = NaCl + C_6H_5 \cdot CH : NO \cdot O \cdot CO \cdot C_6H_5$$
$$\longrightarrow \underset{\text{Dibenzhydroxamic acid}}{C_6H_5 \cdot CO \cdot NH \cdot O \cdot CO \cdot C_6H_5}$$

That these isonitro-compounds contain hydroxyl is shown also by the fact that they react in the cold with phenyl isocyanate, while the nitro-compounds do not.

Similar behaviour is shown by *m*-Nitrophenylnitromethane,  ; the passage from the yellow pseudo-acid to the colourless nitro-compound is clearly shown by the change both in colour and in electrical conductivity, which is very high for the pseudo-acid (as for acids in general) and almost zero for the normal nitro-compound, into which it is gradually converted.

These nitro-derivatives of the side-chain can hence yield metallic derivatives—of the pseudo-acids; treatment of these derivatives with acid yields the normal form, and the latter in presence of alkali is only *slowly* neutralised, this being characteristic of the *pseudo-acids*.

In benzene solution the true acids combine rapidly with ammonia, forming insoluble ammonium salts, while pseudo-acids combine only slowly or not at all with ammonia.

G. AMINO-DERIVATIVES OF AROMATIC HYDROCARBONS

When the hydrogen atoms of benzene are replaced by amino-groups or the hydrogen of ammonia or of a primary aliphatic amine by phenyl groups, the resulting products are *mono-*, *di-*, or *tri-amines* in the first case and *secondary* and *tertiary amines* in the second.

Some of the aromatic amines are similar to but weaker than the aliphatic bases, the phenyl group being somewhat negative in character compared with the positive alkyl groups.

Aromatic amines form salts with acids and double salts with platinum chloride. In contact with the vapours of volatile inorganic acids they form white fumes in the air in the same way as ammonia; they distil undecomposed. The diamines are more highly basic than the monamines.

Isomerides of the amines are formed when the amino group enters side-chains.

1. PRIMARY MONAMINES

Primary, secondary, and tertiary aromatic monamines are distinguished by the same reactions as are used for aliphatic amines (by nitrous acid, etc.; *see* p. 240).

FORMATION. (*a*) Mono-, di-amines, etc., are usually obtained by reducing the nitro-derivatives with tin or stannous chloride and hydrochloric acid, or with iron and acetic acid, or with ammonium sulphide, etc.: $C_6H_5 \cdot NO_2 + 6H = 2H_2O + C_6H_5 \cdot NH_2$. The reduction may also be effected electrolytically (*see later*, diazo-compounds). In the electrolytic reduction of organic compounds in an acid medium, electrodes of lead containing a small proportion of copper are mostly used in place of pure lead electrodes, the resulting products being then purer (Ger. Pat. 252,759, 1911).

(*b*) By heating phenols (or, better, nitrophenols or naphthols) with ammoniacal zinc chloride at 300°, primary amines are readily obtained with small proportions of secondary amines: $C_6H_5 \cdot OH + NH_3 = H_2O + C_6H_5 \cdot NH_2$.

(*c*) By heating secondary and tertiary bases (substituted amines) with

Aromatic Amines

Rational formula	Name	Melting-point	Boiling-point	Specific gravity
$C_6H_5 \cdot NH_2$	Aniline (aminobenzene)	— 8°	184·4°	1·026 at 16°
$CH_3 \cdot C_6H_4 \cdot NH_2$	*o*-Toluidine (1-methyl-2-aminobenzene)	liq.	199°	0·999 at 20°
„	*m*- „ (1- „ -3- „)	liq.	199°	0·998 at 25°
„	*p*- „ (1- „ -4- „)	42·8°	198°	—
$(CH_3)_2C_6H_3 \cdot NH_2$	*o*-Xylidine (*vic.*) (1 : 2-dimethyl-3-aminobenzene)	liq.	223°	0·991 at 15°
„	*o*- „ (*as.*) (1 : 2- „ -4- „)	49°	226°	1·076 at 17°
„	*m*- „ (*vic.*) (1 : 3- „ -2- „)	liq.	215°	—
„	*m*- „ (*as.*) (1 : 3- „ -4- „)	liq.	215°	0·918 at 25°
„	*m*- „ (*s.*) (1 : 3- „ -5- „)	liq.	223°	0·972 at 15°
„	*p*- „ (1 : 4- „ -2- „)	15·5°	215°	0·980 at 15°
$C_2H_5 \cdot C_6H_4 \cdot NH_2$	*p*-Aminoethylbenzene (1-ethyl-4-aminobenzene)	— 5°	214°	0·975 at 22°
$(CH_3)_3C_6H_2 \cdot NH_2$	Mesidine (1 : 3 : 5-trimethyl-2-aminobenzene)	liq.	233°	—
„	Pseudocumidine (1 : 2 : 4-trimethyl-5-aminobenzene)	68°	234°	—
$(C_2H_5 \cdot CH_2) \cdot C_6H_4 \cdot NH_2$	*p*-Aminopropylbenzene (1-propyl-4-aminobenzene)	liq.	225°	—
$(CH_3)_2CH \cdot C_6H_4 \cdot NH_2$	Cumidine (1-isopropyl-4-aminobenzene)	liq.	218°	—
$(CH_3)_4C_6H \cdot NH_2$	Prehnidine (1 : 2 : 3 : 4-tetramethyl-5-aminobenzene)	70°	260°	—
„	Isoduridine (1 : 2 : 3 : 5- „ -4- „)	24°	255°	0·978 at 24°
$(CH_3)(C_3H_7)C_6H_3 \cdot NH_2$	Carvacrylamine (1-methyl-4-propyl-2-aminobenzene)	liq.	241°	0·944 at 24°
„	Thymenamine (1- „ -4- „ -3- „)	liq.	230°	—
$(CH_3)_2CH \cdot CH_2 \cdot C_6H_4 \cdot NH_2$	*p*-Aminoisobutylbenzene (1-γ-methylpropyl-4-aminobenzene)	17°	230°	0·937 at 25°
$(CH_3)_5C_6 \cdot NH_2$	Aminopentamethylbenzene (pentamethylaminobenzene)	152°	278°	—
$C_5H_{11} \cdot C_6H_4 \cdot NH_2$	*p*-Aminoisoamylbenzene	liq.	260°	—
$C_8H_{17} \cdot C_6H_4 \cdot NH_2$	*p*-Aminooctylbenzene (1-octyl-4-aminobenzene)	19·5°	310°	—
$C_{16}H_{33} \cdot C_6H_4 \cdot NH_2$	Aminocetylbenzene (hexadecylaminobenzene)	53°	255 (14 mm.)	—
$C_{18}H_{37} \cdot C_6H_4 \cdot NH_2$	Aminooctodecylbenzene (octodecylaminobenzene)	61°	274 (15 mm.)	—
$C_6H_4(NH_2)_2$	*o*-Phenylenediamine (1 : 2-diaminobenzene)	102°	252°	—
„	*m*- „ (1 : 3- „)	63°	287°	—
„	*p*- „ (1 : 4- „)	147°	267°	—
$CH_3 \cdot C_6H_4(NH_2)_2$	Tolylenediamine 1-methyl-2 : 3-diaminobenzene)	61°	255°	—
„	„ (1- „ -2 : 4- „)	99°	280°	—
„	„ (four other isomerides)	—	—	—
$C_6H_3(NH_2)_3$	Triaminobenzenes	—	—	—

concentrated hydrochloric acid at 180°, $C_6H_5 \cdot N(CH_3)_2 + 2HCl = C_6H_5 \cdot NH_2 + 2CH_3Cl$; at higher temperatures the alkyl chloride reacts with the nucleus, giving homologous amines higher than the original one: $C_6H_5 \cdot NH_2 + CH_3Cl = C_6H_4(CH_3) \cdot NH_2, HCl$. In the same way, trimethylphenylammonium iodide yields mesidine hydriodide, $C_6H_2(CH_3)_3 \cdot NH_2, HI$ (the methyl groups of the nucleus never assume the *meta* position).

PROPERTIES. The primary monamines are liquid or solid and turn brown in the air. With acids they form crystalline salts soluble in water, but with carbonic acid they do not give salts, so that they may be liberated from their salts by means of sodium carbonate. With platinum chloride they form double salts (platinichlorides), *e.g.* $(C_6H_5 \cdot NH_2, HCl)_2, PtCl_4$, which are only slightly soluble and serve for the separation of these bases.

With methyl iodide they form secondary, tertiary, and quaternary compounds: $C_6H_5 \cdot NH \cdot CH_3, HI \rightarrow C_6H_5 \cdot N(CH_3)_2, HI \rightarrow C_6H_5 \cdot N(CH_3)_3I$; the base can easily be separated from the acid by caustic soda.

Benzaldehyde reacts with aniline, forming benzylideneaniline: $C_6H_5 \cdot CHO + C_6H_5 \cdot NH_2 = H_2O + C_6H_5 \cdot CH : N \cdot C_6H_5$, while acetaldehyde gives ethylidene diphenyldiamine:

$$2C_6H_5 \cdot NH_2 + CH_3 \cdot CHO = H_2O + \begin{matrix} C_6H_5 \cdot NH \\ C_6H_5 \cdot NH \end{matrix} > CH \cdot CH_3.$$

The action of the organic acids on amines gives *acianilides*, which are decomposable by alkali:

$$C_6H_5 \cdot NH_2 + CH_3 \cdot COOH = H_2O + \underset{\text{Acetanilide}}{C_6H_5 \cdot NH \cdot C_2H_3O}.$$

When heated with chloroform and alcoholic potash, the primary amines form isonitriles (*carbylamines*), which have most unpleasant odours. With carbon disulphide they give *thioureas*, which with P_2O_5 give mustard oils of the aromatic series.

With nitrous acid (or nitrites) in acid solution, amines yield *diazo-* or *diazoamino compounds*, these giving phenols when boiled with water. Where the amino group is in the side chain, no diazo derivative is formed.

Aniline, *see later*.

2. SECONDARY MONAMINES

These are basic in character, not when they are purely aromatic compounds, but only when they contain also aliphatic radicals. These mixed derivatives are obtained from primary amines by treatment with methyl iodide and, if the acetylated primary base is employed, the simultaneous formation of tertiary base is avoided: $C_6H_5 \cdot NH \cdot COCH_3 + CH_3I = HI + C_6H_5 \cdot N(CH_3)(COCH_3)$; the acetyl group may be removed by subsequent hydrolysis.

The secondary bases may be separated from the tertiary by means of nitrous acid (potassium nitrite), with which the former yield *nitrosamines*: $C_6H_5 \cdot NH \cdot CH_3 + NO \cdot OH = H_2O + C_6H_5 \cdot N(NO) \cdot CH_3$, which are neutral compounds, insoluble in water. When these nitrosamines are heated with hydrochloric acid (alcoholic), the NO group passes into the benzene nucleus: $C_6H_5 \cdot N(NO) \cdot CH_3$ gives $C_6H_4(NO) \cdot NH \cdot CH_3$.

Pure aromatic secondary monamines are obtained by heating the primary bases with the corresponding hydrochlorides:

$$C_6H_5 \cdot NH_2 + C_6H_5 \cdot NH_2, HCl = (C_6H_5)_2NH + NH_4Cl.$$

3. TERTIARY MONAMINES

These are formed by alkylating primary or secondary bases.

Triphenylamine is obtained from bromobenzene by the action of dipotassio-aniline: $2C_6H_5Br + C_6H_5 \cdot NK_2 = 2KBr + (C_6H_5)_3N$.

The purely aromatic tertiary monamines are not basic in character, and

hence do not form salts. They do not give isonitriles with chloroform, or mustard oils with CS_2.

With alkyl iodides they form quaternary compounds. When they are treated with nitrous acid, the NO group enters the benzene nucleus, this reaction distinguishing these bases from the tertiary bases of the fatty series.

4. QUATERNARY BASES

These are analogous to the corresponding aliphatic compounds. **Trimethylphenylammonium hydroxide**, $C_6H_5 \cdot N(CH_3)_3OH$, for example, is strongly alkaline, colourless, and bitter, and is decomposed on heating.

5. DIAMINES, TRIAMINES, TETRAMINES, ETC.

These are obtained by reducing the corresponding nitroamino- or polynitro-derivatives; thus **tetraminobenzene** is formed from dinitro-*m*-diaminobenzene.

The polyamines give various reactions with nitroso-compounds of tertiary amines, with certain azo-dyes, etc.

The diamines and polyamines are solid substances, which distil undecomposed and are soluble in hot water. They are colourless, but turn brown in the air with a rapidity increasing with the number of amino-groups; they give characteristic colorations with ferric chloride.

The **ORTHODIAMINES** form **Anhydro-bases** or **Benziminazoles**, *e.g.*, $C_6H_4 \Big< \begin{matrix} NH \\ N \end{matrix} \Big> C \cdot CH_3$. Further, aldehydes react with the hydrochlorides of diamines, forming **Anhydro-bases** or **Aldehydo-bases**.

Glyoxal yields **Quinoxaline**, etc., while nitrous acid gives **Azimino-compounds**, *e.g.*, **Aziminobenzene** (*aminoazophenylene*), $C_6H_4 \Big< \begin{matrix} NH \\ N \end{matrix} \Big\rangle\!\!\!\!\!\!\;\; N$.

m-**DIAMINES** give, with nitrous acid, yellowish brown colouring-matters (*Bismarck brown*: sensitive reaction). With diazobenzene chloride they yield azo-dyes (*chrysoidine*). When oxidised together with *p*-diamines, they give a blue colour which becomes red on boiling.

p-**DIAMINES**, when oxidised with $MnO_2 + H_2SO_4$, yield quinone, $C_6H_4O_2$, and a homologue with a peculiar odour; some of them give colouring-matters when treated with solutions of hydrogen sulphide and ferric chloride.

ANILINE (Aminobenzene, Phenylamine), $C_6H_5 \cdot NH_2$.[1]

Industrially it is prepared by treating nitrobenzene with nascent hydrogen produced by the action of hydrochloric acid on iron filings or, better, turnings, as was proposed in 1864 by Béchamp, who first used acetic acid in place of hydrochloric:

$$C_6H_5 \cdot NO_2 + 6HCl + 3Fe = C_6H_5 \cdot NH_2 + 3FeCl_2 + 2H_2O.$$

The quantity of HCl consumed is, however, only one-fortieth of the theoretical amount, so that after a certain point the reduction is perhaps continued by the action of the iron on water in presence of ferrous chloride: $2Fe + C_6H_5 \cdot NO_2 + 4H_2O = 2Fe(OH)_3 + C_6H_5 \cdot NH_2$. The apparatus for manufacturing aniline consists of a cast-iron cylinder, *A* (Fig. 446), the lower half of which is furnished with a discharge tap and is replaceable, as it corrodes rapidly; it is provided with a cover, through which pass a vertical stirrer, *B*,

[1] Aniline was discovered in 1826 by Unverdorben among the products of the dry distillation of indigo and was called *crystalline*, since with acids it readily formed crystalline masses. It was then found also by Runge in 1834 in coal-tar, and he named it *kyanol* or *blue oil*, since with hypochlorite it gave a blue coloration and its salts a violet coloration.

In 1841 Fritsche obtained it by distilling indigo with potash, and he termed it, after the native name of the plant, "*anil*," *aniline*. In 1842 Zinin gave the name *benzidam* to the product obtained by reducing nitrobenzene with ammonium sulphide. The identity of these various substances and their true constitution was proved by Hofmann in 1843.

worked by toothed wheels, and a direct-steam coil. The cover is also fitted wit
condenser, *NOG*, and a hopper, *F*, with a wooden plug for the introduction o
turnings. A tube fixed laterally to the lower part of the reflux condenser carr
aniline distilling with the steam to a condensing coil, *O*, and a receiver, *R*. The
is carried out as follows: 300 litres of water, 180 kilos of iron turnings, and 60 k
centrated hydrochloric acid are kept stirred in the cylinder while 750 kilos of ni
are introduced. The reaction is started by a jet of direct steam, and is afterw
tained by gradually adding moist iron turnings up to a total quantity of 650 ki
additions are made over a period of 6 to 7 hours and are arranged so that
is kept hot (90° to 95°), but the reaction is allowed to calm down before fresh ir
duced. If the reaction becomes violent, benzene and ammonia are formed instead
A further quantity of 100 to 150 kilos of iron turnings is added. The nitrobenzene
ing with the water is condensed in the reflux condenser. At the end of the
the vessel contains aniline, aniline hydrochloride, ferric oxide and *o*- and *p*
together with a little unaltered nitrobenzene and some impurities such as azob
Thick milk of lime is then added until the reaction is strongly alkaline, and the

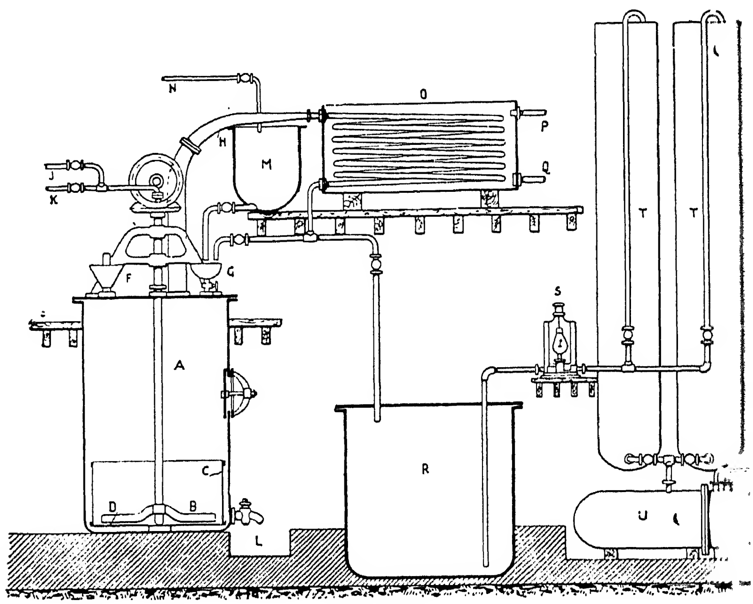


FIG. 446.

tilled with superheated direct steam. The distillate condensed in *R* separates
layers, the lower one of aniline and the upper one of water containing 2 to 3 pe
aniline in suspension or solution; this lower layer is used in the reduction of ne
quantities of nitrobenzene. The decanted aniline is purified by distillation *in va*
an iron still. The decomposition of the aniline hydrochloride by milk of lime ta
according to the equation:

$$2C_6H_5 \cdot NH_2, HCl + Ca(OH)_2 = CaCl_2 + 2H_2O + 2C_6H_5 \cdot NH_2.$$

It has also been proposed (Ger. Pat. 184,809) to reduce nitrobenzene by
sodium bisulphite in the hot.

At one time the nitrobenzene employed was obtained from crude 90 per cent
containing toluene, the resultant product being a mixture of aniline and toluidi
served well for the preparation of certain dyes, but nowadays it is regarded as
to start from pure benzene and pure toluene separately and to mix the aniline and
subsequently in the required proportions.

Aniline can also be obtained by other processes which have not yet been a
a large scale, *e.g.*, by passing a mixture of nitrobenzene vapour with excess of
(or water-gas) over reduced copper turnings heated to 300° to 400°; the copp
a catalyst and remains unchanged (Ger. Pat. 139,457). Some importance is

assumed by the electrolytic process, according to which nitro derivatives can be converted into amino derivatives in presence of metallic salts (*e.g.*, copper salts), which also separate at the cathode (*see* Diazo compounds).

Kunz's process, based on reduction of nitrobenzene by means of sodium bisulphide, $C_6H_5NO_2 + Na_2S_2 + H_2O = C_6H_5NH_2 + Na_2S_2O_3$, gives a good yield and allows of the separation of pure sodium thiosulphate by concentration of the residual aqueous solution.

Aniline is a liquid which boils at 184·4° (92° at 33 mm. pressure), has the sp. gr. 1·026 at 16°, and solidifies at −6·3° (or −20° if impure). It is colourless and refractive (refractive index, 1·585 at 20°), but becomes brown in the air at a rate increasing with the proportion of impurities present. It is soluble in alcohol, ether, benzene, fatty oils and, to a slight extent (3 per cent., whilst aniline dissolves 5 per cent. of water) in water, and it dissolves sulphur (in the hot), phosphorus, camphor, indigo, a little water (in the hot), etc.; it is readily oxidisable. It distils easily and completely in steam, and its vaopur is somewhat poisonous [1] and combustible. As a base it is weaker than ammonia in the cold but stronger in the hot, but its aqueous solution does not react with litmus or turmeric paper. Although it is a weak base, it precipitates salts of zinc, aluminium, and iron, and in the hot it displaces ammonia from various salts.

With formaldehyde it gives a characteristic (for aniline and for the aldehyde) condensation product $(C_6H_5 \cdot N:CH_2)_3$, melting at 40°. With chloride of lime a solution of aniline becomes intensely blue if pure or violet if impure (sensitive reaction), the colour rapidly changing to brown; if the aniline solution is very dilute this coloration does not appear, but a red colour will then form on further addition of a few drops of ammonium hydrosulphide, minimal traces (1 : 250,000) of aniline being thus detectable. Aniline or one of its salts forms *p*-aminobenzenesulphonic acid with concentrated sulphuric acid, but in presence of a drop of potassium dichromate solution a fine blue colour is produced which disappears very rapidly; in dilute solution a green and then a black colour (aniline black) is formed. Different methods of oxidising aniline give varied products: azobenzene, nitroso- and nitro-benzene, *β*-phenylhydroxylamine, *p*-aminophenol, quinone, *p*-aminophenylamine, violaniline (with arsenic acid). Oxidation of a mixture of aniline and toluidine yields fuchsine, while a mixture of aniline and *p*-toluylenediamine gives safranine.[2] Chlorine transforms dry aniline into a tarry substance, while in presence of water trichloraniline and trichlorophenol are formed. The action of calcium hypochlorite on a solution of aniline in chloroform yields azobenzene.

Some of the more important salts and derivatives of aniline and its homologues are as follow:

ANILINE HYDROCHLORIDE (Aniline salt), $C_6H_5 \cdot NH_2, HCl$, is obtained pure and dry in white crystals by passing a current of dry hydrogen chloride into an ethereal solution of aniline. It melts at 198° and partly sublimes, and boils unchanged at 245°; it dissolves readily in water or alcohol, but is insoluble in ether.

It is prepared industrially by neutralising aniline at 100° with concentrated hydrochloric acid, free from chlorine. After standing for some days, crystalline aniline salt separates out, this being centrifuged and dried at 50°; the mother liquors are then evaporated and crystallised. In the air the white scales assume a reddish or greenish tint. In presence of HCl its aqueous solution imparts a yellow colour to pine wood or elder-pith.

[1] Aniline acts on the nervous system, and even when its action is slight the edges of the lips are turned bluish and an effect similar to drunkenness is produced, but the face becomes pale and the appetite fails; in such cases Epsom salts are administered as purgative, alcoholic liquors being harmful. Clothes soaked in aniline may produce serious poisoning and giddiness so acute as to cause collapse, the lips becoming dark blue or even black. When this happens, recourse should be had to excitants or ablution or to small doses of ether administered internally. Benzene and nitrobenzene vapours are also injurious to health.

[2] For the making of aniline black and other dyes, the following qualities of aniline are placed on the market: *aniline oil for blue*, which is almost pure aniline, b.-pt. 182° to 186°, sp. gr. 1·034 to 1·036; *aniline oil for red*, consisting of about 1 part of aniline and 2 parts of *o*- and *p*-toluidines and boiling at 190° to 198°; *aniline oil for safranine*, sp. gr. 1·032 to 1·034, containing 35 to 50 per cent. of aniline and 50 to 65 per cent. of *o*-toluidine. Aniline oil is tested commercially by measuring the fractions distilling at different temperatures from 100 grms. of the oil in a suitable distilling flask fitted with a thermometer graduated in fifths of a degree from 150° to 225°, the heating being carried out on a sand bath. The best qualities of aniline oil give 95 to 98 per cent. of distillate between 182° and 185°. It is also advisable to make small dyeing tests with aniline black in order to ascertain which of the different aniline oils and salts on the market gives the finest and most intense black (*see later*, Dyeing Processes).

ANILINE SULPHATE, $(C_6H_5 \cdot NH_2)_2, H_2SO_4$, is only slightly soluble in water.

Various other salts of organic and inorganic acids are known.

ANILINE PLATINICHLORIDE, $(C_6H_5 \cdot NH_2, HCl)_2, PtCl_4$, forms yellow leaflets dissolving readily in water and, to a less extent, in alcohol.

METHYLANILINE, $C_6H_5 \cdot NH \cdot CH_3$, is obtained by heating 100 parts of aniline hydrochloride with 30 parts of methyl alcohol (free from acetone) at 180° in an enamelled iron autoclave. It is a colourless liquid, sp. gr. 0·972 at 15°, b. pt. 193·8°, with an odour resembling, but stronger than, that of aniline. With chloride of lime it gives first a violet and then a brown coloration. The corresponding **NITROSAMINE,** $C_6H_5 \cdot NO \cdot CH_3$, is obtained by methylating phenylnitrosamine or by treating methylaniline with nitrous acid. It forms a yellow oil which distils unchanged only in a current of steam and gives Liebermann's reaction, characteristic of the nitrosamines and of various nitroso derivatives; this reaction consists in the formation of a dark blue coloration when the nitroso compound is heated with phenol and sulphuric acid and the liquid then diluted with water and neutralised with potash.

DIMETHYLANILINE, $C_6H_5 \cdot N(CH_3)_2$, is a mixed tertiary amine and is obtained by heating aniline hydrochloride with methyl alcohol, methyl chloride being formed as an intermediate product and reacting with the aniline. If, however, dimethylaniline hydrochloride is heated with gaseous hydrogen chloride at 180°, methyl chloride and aniline are formed. When dimethylaniline is heated to a high temperature, the alkyl groups pass into the nucleus. The hydrogen in the para position of these dialkylamines is readily replaceable by different groups; thus, the action of nitrous acid yields *p-nitrosodimethylaniline*, which forms green crystals and gives a yellow hydrochloride. Permanganate converts the NO group into NO_2, giving *nitrodimethylaniline* (m. pt. 162°), while boiling with caustic soda results in the elimination of dimethylamine and the formation of *nitrosophenol*, $NO \cdot C_6H_4 \cdot OH$. It gives a straw yellow coloration with chloride of lime and reacts with aldehydes and various other compounds.

Dimethylaniline, which is of importance owing to its use in the manufacture of various dyes, is a colourless, oily liquid, solidifying at 2·5°, b. pt. 192·5°, density 0·962 at 15°. The pure compound falls in temperature when mixed with an equal weight of acetic anhydride, whereas if aniline or monomethylaniline is present the temperature rises.

DIPHENYLAMINE, $C_6H_5 \cdot NH \cdot C_6H_5$, is obtained by heating aniline with its hydrochloride in an autoclave at 220° to 230° for 10 hours:

$$C_6H_5 \cdot NH_2, HCl + C_6H_5 \cdot NH_2 = NH_4Cl + C_6H_5 \cdot NH \cdot C_6H_5.$$

Contardi (1918) developed a method which requires no autoclave and may be rendered almost continuous.

Diphenylamine melts at 54° and boils at 302°, and forms a very sensitive reagent for the detection of traces of nitric acid, with which, in presence of concentrated sulphuric acid, it gives an intense blue coloration (also given with nitrous acid and various oxidising agents; *see* Detection of Nitrates in Water, Vol. I., p. 234). It is also largely used to stabilise smokeless nitrocellulose powders (4 to 6 per cent.) and gelatine dynamites, and serves also in the manufacture of orange IV., metanil yellow, diphenyl blue, etc.

DIPHENYLCHLOROARSINE, $NH\begin{matrix} C_6H_4 \\ \\ C_6H_4 \end{matrix}AsCl$, known as Adamsite or DM, forms a yellowish, crystalline mass, m. pt. 193°, and was largely used in poison shells during the war, 0·012 grm. rendering 30 cu. m. of air irrespirable. It is prepared by heating either diphenylamine with arsenic trichloride for 24 hours at 160° to 190° in a reflux apparatus or diphenylamine hydrochloride with arsenious anhydride.

Various nitro- and nitroso derivatives are known, as well as *triphenylamine*, $N(C_6H_5)_3$, which crystallises in large plates melting at 127° and distils unchanged.

BENZYLANILINE (Benzylphenylamine), $C_6H_5 \cdot CH_2 \cdot NH \cdot C_6H_5$, is obtained either by heating benzyl chloride (1 mol.) with aniline (2 mols.) or by reducing *thiobenzanilide*, $C_6H_5 \cdot CS \cdot NH \cdot C_6H_5$. It forms crystals melting at 33° and boils at 310°.

HEXANITRODIPHENYLAMINE, $NH\left(\begin{matrix} NO_2 \\ \qquad NO_2 \\ NO_2 \end{matrix}\right)_2$, is a yellow colouring matter (*aurantia* is its ammonium derivative, $NH_4 \cdot N[C_6H_2(NO_2)_3]_2$), but is prepared in large quantities as a shattering explosive for charging torpedoes. In its manufacture 2 : 4-

dinitrochlorobenzene is treated with aniline, giving *dinitrodiphenylamine*, $C_6H_5 \cdot NH \cdot C_6H_3(NO_2)_2$, m.-pt. 157°. Nitration of the latter yields *tetranitrodiphenylamine*, m.-pt. 180° to 190°, and nitration of this *hexanitrodiphenylamine*, m.-pt. 240° to 250° (decomp.); this compound is turned brown by sunlight, is somewhat sensitive to shock, and inflames the skin and irritates the mucus of the eyes.

PHENYLSULPHAMINIC ACID, $C_6H_5 \cdot NH \cdot SO_3H$, is obtained by the action of sulphur trioxide on the amine, and is very unstable except in the form of salts.

ANILIDES are derivatives of aniline in which one or both of the hydrogen atoms of the amino-group of aniline are replaced by one or two inorganic or organic acid residues; in the latter case, compounds of considerable interest are formed.

FORMANILIDE, $C_6H_5 \cdot NH \cdot CHO$, obtained by heating aniline with formic acid, melts at 46° and is used for making *p-nitroaniline*.

ACETANILIDE (Antifebrin), $C_6H_5 \cdot NH \cdot COCH_3$, is obtained by boiling a mixture of aniline and glacial acetic acid for a couple of days in an earthenware vessel fitted with a reflux condenser:

$$C_6H_5 \cdot NH_2 + CH_3 \cdot CO \cdot OH = H_2O + C_6H_5 \cdot NH \cdot COCH_3.$$

Industrially it is made in thick, seamless, aluminium vessels placed in iron vessels to protect them from direct fire heat. It is purified by repeatedly crystallising or distilling, best *in vacuo*. It melts at 115° and boils at 303·8°, with partial sublimation at 95°. It dissolves in 174 parts of cold or 18 parts of boiling water or in $3\frac{1}{2}$ parts of alcohol; it is readily soluble in ether or chloroform. The hydrogen atom united to nitrogen can be replaced by metals (Na, K, etc.). It causes considerable lowering of the temperature of animal organisms, and is hence used as an antipyretic. It may be used to replace camphor in making celluloid, and is employed also to adulterate certain perfumes (vanillin, musk, piperonal, etc.).

Di- and Tri-acetanilides have analogous properties, and **Methylacetanilide**, $C_6H_5 \cdot N(CH_3) \cdot COCH_3$, is used under the name of *exalgin* as a specific against headache. *Diacetanilide* melts at 37°.

CHLORACETANILIDE, $C_6H_4Cl \cdot NH \cdot COCH_3$, exists in three isomeric forms: the ortho-compound, melting at 88°; the meta-, at 72·5°; and the para-, at 172°. The chloro- and bromo-derivatives of acetanilide and other anilides are obtained by the action of chlorine or bromine on the anilide or by the interaction of acetyl chloride and the substituted anilines. Another series of isomerides is that in which the substitution is in the acid group, *e.g.*, **Phenylchloracetamide**, $C_6H_5 \cdot NH \cdot CO \cdot CH_2Cl$ (m.-pt. 134°), which is obtained from chloracetyl chloride and aniline. Phenyldichlor- (m.-pt. 118°) and phenyltrichloracetamide (m.-pt. 82°) are also known.

NITRACETANILIDE, $NO_2 \cdot C_6H_4 \cdot NH \cdot COCH_3$. The three isomerides are obtained by the action of acetyl chloride on the corresponding nitranilines; the *o*-compound melts at 92° (yellowish crystals), the *m*- at 142°, and the *p*- at 207°.

PHENYLACETANILIDE (Diphenylacetamide), $(C_6H_5)_2N \cdot CO \cdot CH_3$, is obtained by treating a benzene solution of diphenylamine with acetyl chloride; it melts at 99·5°.

BENZANILIDE (Phenylbenzamide), $C_6H_5 \cdot NH \cdot COC_6H_5$, is prepared from benzoyl chloride and aniline and melts at 162°. It is very stable, but is decomposed by fusion with alkali. It is insoluble in water, but dissolves in alcohol.

PHENYLGLYCOCOLL (Phenylaminoacetic or Anilidoacetic acid), $C_6H_5 \cdot NH \cdot CH_2 \cdot CO_2H$, is obtained by protracted heating of chloroacetic acid (1 mol.) and aniline (2 mols.) with water. It forms crystals melting at 127°, gives characteristic mercury and copper salts, and when heated at 150° gives up water and yields the anhydride $C_6H_5 \cdot N{<}\begin{matrix}CH_2\\ |\\ CO\end{matrix}$, melting at 263°.

HOMOLOGUES OF ANILINE, POLYAMINES, AND THEIR DERIVATIVES

(*see* Table, p. 655).

ORTHO- and PARA-TOLUIDINES, $CH_3 \cdot C_6H_4 \cdot NH_2$, are obtained by reducing the corresponding nitro-compounds. Since the three isomerides are formed simultaneously in the nitration of toluene, reduction yields a mixture of the three toluidines (*m*-toluidine in small amount). In order to separate them, the mixture is poured into a solution of oxalic acid containing hydrochloric acid and the liquid heated to boiling; the *p*-toluidine oxalate, which is only slightly soluble in water and insoluble in ether, is then separated,

the filtrate containing the soluble hydrochlorides of the other toluidines. Also Wülfing has shown that only amines which have the para-position free can be converted (by HCl + $NaNO_2$) into the corresponding aminoazo-derivatives, the unaltered *p*-toluidine being then separable by distillation in steam. *p*-Toluidine can also be separated by cooling, since it freezes first. The toluidines are distinguished from aniline by the different solubilities of the nitrates, hydrochlorides, and acetyl-derivatives. *p*-Toluidine, like the meta-compound, costs double as much as the ortho-isomeride. *o-Toluidine*, which is also found in coal-tar, is a liquid (sp. gr. 1·09) boiling at 199° and turning brown in the air. *p-Toluidine* is a solid melting at 43°, and boils at 198°; it is sparingly soluble in cold water, but dissolves readily in alcohol, ether, or benzene. The toluidines are used in the manufacture of dyes.

m-**TOLUIDINE** is obtained indirectly by nitrating acetylated p-toluidine, the compound  being thus formed; the acetyl-group is then eliminated by boiling with hydrochloric acid and the amino-group by diazotisation. Reduction of the resultant *m*-nitrotoluene yields *m*-toluidine, which is a colourless oil (sp. gr. 0·998 at 25°) boiling at 197°.

XYLIDINES. Six isomerides are known (*see* Table, p. 655), and all are formed together by nitrating crude xylene and reducing the resulting nitro-compounds; the most important is *m*-xylidine. Various methods of separating the different xylidines are known, almost all of them being patented and based on the varying solubilities of the acetates and hydrochlorides of *p*- and *m*-xylidines. The separate isomerides are prepared pure from the corresponding pure nitro-compounds.

BENZYLAMINE, $C_6H_5 \cdot CH_2 \cdot NH_2$, is isomeric with the toluidines and behaves like the amines of the aliphatic series. It is obtained together with di- and tri-benzylamine by heating benzyl chloride with ammonia. It is a colourless liquid of ammoniacal odour and boils at 185°; it has an alkaline reaction and is a more energetic base than aniline, the amino-group being further removed from the benzene nucleus, which has a somewhat negative (acid) influence.

o-**PHENYLENEDIAMINE**, $C_6H_4(NH_2)_2$, m.-pt. 102°, b.-pt. 257°, obtained by reducing *o*-nitroaniline with caustic soda and zinc dust, is of little practical importance.

m-**PHENYLENEDIAMINE**, m.-pt. 63°, b.-pt. 287°, is made by reducing *m*-dinitrobenzene with iron turnings and hydrochloric acid. With a trace of a nitrite and hydrochloric acid it gives the characteristic brownish-yellow coloration of Bismarck brown. It is used as a developer in dyeing and printing cotton, but more especially for making numerous azo and other dyes, *e.g.*, Bismarck brown, anthracene acid brown B, Columbia black FB, FT, vesuvine, azo bordeaux, chrysoidine, diamine brown V, neutral violet.

p-**PHENYLENEDIAMINE** is obtained by the reduction of aminoazobenzene (dissolved in aniline) with hydrogen sulphide, or hydrochloric acid and iron turnings, or, more easily, by heating *p*-dichlorobenzene or *p*-chloraniline with ammonia in presence of a copper salt (Ger. Pat. 204,408), or by reducing *p*-nitroaniline with hydrochloric acid and iron turnings.

It melts at 147°, boils at 267°, and is soluble in alcohol or ether, and to a less extent in water; in the air it browns slightly. Addition of a trace of its hydrochloride and then a few drops of ferric chloric solution to dilute hydrogen sulphide solution gives a characteristic violet coloration (*Lauth's violet*).

It is used in making many dyes: ethyl acid violet, azidine orange, brown and black, azoalizarin black, direct brown R, paraphenylene blue and violet, etc. With raw, but not with boiled, milk it gives a violet coloration. It colours woody fibre brick-red, and has been proposed as an accelerator of the vulcanisation of rubber. It is frequently employed for *dyeing hair* by oxidising it with hydrogen peroxide, but its use for this purpose should be prohibited owing to its poisonous properties.

TOLYLENEDIAMINES, $C_6H_3(CH_3)(NH_2)_2$. The most common of these is the *o* : *p*-compound, *i.e.*, the one with the amino-groups in the 2 and 4 positions and the methyl group in the position 1. It is obtained by reducing the corresponding dinitrotoluene (*see* p. 651) with iron and hydrochloric acid and is used for making dyes and, together with sodium sulphite, for dyeing hair, as it does not seem to be injurious to health, as *p*-phenylenediamine is. It costs about 16*s*. per kilo.

NITROANILINES. Concentrated nitric acid acts very energetically on aniline, and in order that the nitro-groups may be introduced into the benzene nucleus without the amino-group being attacked, either the amino-group is acetylated or the nitration is carried out in presence of a large proportion of concentrated sulphuric acid.

o-NITROANILINE, $NO_2 \cdot C_6H_4 \cdot NH_2$, forms orange-yellow crystals, m.-pt. 71·5°, and is obtained by heating *o*-chloronitrobenzene with concentrated ammonia solution under pressure. It is of little industrial importance.

m-NITROANILINE, prepared by reducing *m*-dinitrobenzene with sodium polysulphides, forms yellow crystals, m.-pt. 114°, dissolves in water to the extent of 7·12 per cent., and is used for making alizarin yellow GG and dimethylnitraniline orange.

p-NITROANILINE is made either by heating *p*-nitrochlorobenzene with ammonia under pressure, or by nitrating acetanilide to *p*-nitroacetanilide and hydrolysing the latter. It forms yellow crystals, m.-pt. 147°, dissolves to the extent of 0·08 per cent. in water and 5·84 per cent. in alcohol, and is used for making alizarin yellow R, *p*-nitraniline red and *p*-phenylenediamine.

2 : 4-DINITROANILINE, obtained by heating 2 : 4-dinitrochlorobenzene with concentrated ammonia under pressure, forms yellow crystals, m.-pt. 188°, and serves for making violet G for wool and permanent red 2G. The presence of the two nitro groups attenuates the basic character of the amino group, which is diazotised only in concentrated sulphuric acid solution.

s- (2 : 4 : 6-) TRINITROANILINE (PICRAMIDE), $NH_2 \cdot C_6H_2(NO_2)_3$, obtained from picryl chloride and ammonia, forms orange-red needles, m.-pt. 186° ; it has not been diazotised.

2 : 3 : 4 : 6-TETRANITROANILINE, m.-pt. 210°, prepared by nitrating *m*-nitroaniline, is a more powerful explosive than other aromatic nitro-compounds but less so than nitroglycerine. Characteristic is the mobility and hence the ready replaceability of the nitro-group in position 3.

TRINITROPHENYLMETHYLNITROAMINE (Tetryl), $C_6H_2(NO_2)_3 \cdot N(NO_2) \cdot CH_3$, prepared by nitration of dimethylaniline, forms yellow crystals, m.-pt. 129°, and is an endothermic compound (— 40·8 cals.). It is a highly stable compound but is more sensitive to shock than picric acid, and is used as a secondary detonator.

H. NITROPHENOLS, AMINOPHENOLS

NITROPHENOLS. The ortho- and para-compounds are obtained mixed by treating phenol with dilute nitric acid, a larger proportion of the para-derivative being formed in the cold and of the ortho- in the hot. The latter is volatile in steam, and can hence be readily separated from the former.

m-Nitroaniline gives *m-nitrophenol* only by passing through the diazo-compound, but *o*- and *p*-nitroanilines give the corresponding nitrophenols when simply fused with potash.

Nitrophenols are more markedly acid than the phenols and decompose the alkali carbonates, forming **Nitrophenoxides.**

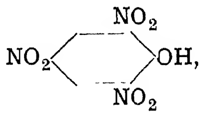
o-NITROPHENOL, free from the para-isomeride, is obtained by distilling *o-nitro-p*-phenolsulphonic acid in steam superheated to 150°, or by heating *o*-chloronitrobenzene with sodium carbonate solution, or by boiling *o*-nitrobenzene with caustic soda. It forms yellow crystals with a peculiar aromatic odour, sp. gr. 1·447, m.-pt. 44·5 to 45°, b.-pt. 214°. It forms orange-red salts ; when heated at 200° with methyl sulphate and methyl alcohol, the sodium salt gives *o-nitrophenol methyl ether*, which, on alkaline reduction, yields dianisidine, this being used for making azo dyes.

m-NITROPHENOL, prepared from *m*-nitraniline and nitrous acid, forms yellow crystals, m.-pt. 96°, b.-pt. 194° (*in vacuo*), and is not volatile in steam.

p-NITROPHENOL, colourless needles, m.-pt. 114°, is used especially in making phenacetin (*q.v.*), and is obtained by heating *p*-nitraniline with caustic soda solution.

p-NITROPHENETOLE, which is the ethyl ether of *p*-nitrophenol, $NO_2 \cdot C_6H_4 \cdot OC_2H_5$, forms crystals, m.-pt. 58°, b.-pt. 283°, and is used in making *p*-phenetidine (*q.v.*). It is prepared by mixing *p*-nitrophenol, alcohol and 50 per cent. caustic soda solution, allowing to cool overnight, and heating under pressure with ethyl chloride and alcohol.

DINITROPHENOLS, $OH \cdot C_6H_3(NO_2)_2$. Various isomerides are known. The 2 : 4-compound is used for making colouring matters, especially *sulphur black*, and was made in large quantities during the war for mixing with picric acid to lower its melting-point. It is obtained by nitrating chlorobenzene and treating the resultant dinitrochlorobenzene with sodium carbonate. It is used also for preserving timber. It melts at 114° and has the sp. gr. 1·683. Tin and hydrochloric acid convert it into 2 : 4-diaminophenol (*amidol*), while with ammonium sulphide it gives 4-nitro-2-aminophenol, and with toluene-*o*-sulphochloride 1-chloro-2 : 4-dinitrobenzene.

PICRIC ACID (Trinitrophenol),  was discovered in 1771 by Amato di Welter, but was used first as a dye and much later as an explosive. It is formed by the action of concentrated nitric acid on various substances, such as silk, wool, indigo, certain resins, etc., and by the oxidation of *s*-trinitrobenzene with potassium ferricyanide. Further nitro-groups cannot be introduced directly into picric acid.

The first tests on its explosive properties were made by Sprengel in 1871, and on Turpin's representations it was applied by the French Government under the name *melinite* (*see* p. 303) for charging grenades.

Before the war it was prepared industrially as follows: equal weights of sulphuric acid (66° Bé.) and pure phenol were heated at 120° in a cast-iron vessel and continually stirred until a small portion of the mass dissolved in water without separation of phenol. The phenolsulphonic acid thus obtained was poured into two parts of cold water and the solution introduced gradually into earthenware jars containing 65 per cent. nitric acid (sp. gr. 1·400) in the proportion of 3·5 parts per 1 part of phenol. The jars were surrounded by a water-bath and were covered over so that the nitrous fumes, which were at first freely evolved, could be drawn off. Towards the end of the reaction the water-bath was heated to boiling. The stages of the process are represented by the following equations:

$$(1)\ C_6H_5 \cdot OH + H_2SO_4 = H_2O + OH \cdot C_6H_4 \cdot SO_3H;$$
$$(2)\ OH \cdot C_6H_4 \cdot SO_3H + 3HNO_3 = 2H_2O + H_2SO_4 + OH \cdot C_6H_2(NO_2)_3.$$

When the mass is cool it solidifies, and it was then centrifuged and washed with a little water; by this means the picric acid crystals can be efficiently separated from the mother-liquor.

During the European War it was prepared on a large scale by treating pure synthetic phenol with sulphuric acid, and nitrating the resultant phenoldi- (and tri-) sulphonic acid by means of sodium nitrate and nitric acid.

A suggestion has been made to prepare picric acid in the cold, as follows (Fr. Pat. 345,441): 1 part of crude phenol is stirred into a mixture of 10 parts of nitric acid (sp. gr. 1·4) with 3 parts of denatured alcohol, the mass being poured into hot water at the end of the reaction; the yield is good, but part of the alcohol is oxidised and lost. When phenol is dear, aniline is sometimes used, being converted into the sulphonic acid, diazotised, and treated with the theoretical quantity of nitric acid (Ger. Pat. 125,096).

PROPERTIES. Picric acid forms yellowish, very bitter, and somewhat poisonous leaflets, which melt at 122·5° and have the sp. gr. 1·7635 or, in the fused state, 1·62 to 1·64. It burns without exploding, but if it is heated in a closed vessel, or if its vapour is superheated, it may explode with great violence. In the open, mercury fulminate is not able to explode it, a detonator of dry guncotton (or lead picrate) with a mercury fulminate cap being necessary. When it is exploded in a closed vessel, its shattering effect is double that of dynamite.

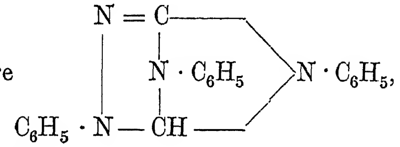
One hundred parts of water dissolve 0·626 part of picric acid at 5°, 1·161 part at 15°, 1·225 part at 20°, or 3·89 parts at 77°. It is readily soluble in alcohol or benzene. In aqueous solution it is dissociated to some extent and shows a marked acid action. The yellow colour of its aqueous solution is due to the anion; in light petroleum it gives a colourless solution, and is hence non-ionised.

It is non-volatile in steam. Its hydroxyl-group is highly reactive, owing to the presence of the three nitro-groups. The potassium and ammonium salts are exploded by percussion, whilst the free acid requires a detonator.

With many aromatic hydrocarbons it forms well-crystallised, molecular compounds which serve for the identification and separation of the hydrocarbons; picric acid is eliminated from these compounds by ammonia.

When reduced with tin and hydrochloric acid it yields 2 : 4 : 6-*triaminophenol*, whilst with ammonium sulphide or sodium hydrosulphide, or on electrolysis (in presence of vanadium salts) it gives 4 : 6-*dinitro-2-aminophenol* (*picramic acid*).

With potassium cyanide it gives a characteristic and sensitive red coloration (*isopurpuric acid*). With nitron acetate it gives a precipitate of nitron picronitrate, $C_{20}H_{16}N_4$, $C_6H_3O(NO_2)_3$, which is insoluble in extremely dilute aqueous solutions acidified with sulphuric acid, and can be filtered off, washed with water, dried at 110°, and weighed.

Nitron has the structure , and in presence of acetic acid precipitates NO_3 ions from very dilute solutions even when nitrites are also present.

With calcium hypochlorite picric acid forms chloranil (p. 648) and chloropicrin (p. 236), the yellow stain of the acid being removable from fabrics or the hands in this way.

The decomposition of picric acid on explosion has not been thoroughly investigated, but is represented approximately by the equation:

$$C_6H_2(OH)(NO_2)_3 = 6CO + H_2O + 3N + H;$$

the acid is hence too poor in oxygen to give the maximum effect, the carbon monoxide and hydrogen not being oxidised.

USES. Picric acid is employed in the preparation of certain organic compounds and was at one time used for dyeing silk and wool yellow, but the colour is not very stable; it has also been used for colouring foodstuffs. It is now mostly used as an explosive, either as acid or in the form of ammonium or potassium salt, these exploding at 310° or on percussion (*see* Explosives, pp. 258 *et seq.*). *Melinite*, a very powerful explosive suggested by Turpin for filling grenades, is merely picric acid which has been fused in a tinned vessel; it is poured into the empty grenade, the interior of which is also tinned. A cold saturated aqueous solution of picric acid is used for alleviating the pains of burns.

From ammonium picrate and ammonium salts of trinitrocresol, sometimes with addition of potassium nitrate, powerful and stable explosives are obtained, these bearing various names (*lyddite*, *ecrasite*, etc.).

TRINITRORESORCINOL, $C_6H(OH)_2(NO_2)_3$, has also been proposed as an explosive.

AMINOPHENOLS. *o*-Aminophenol, $NH_2 \cdot C_6H_4 \cdot OH$, forms colourless crystals which turn brown and resinify in the air; it melts at 174° and sublimes. Its acid properties are weak and it forms salts only with acids. With ferric chloride it gives a red coloration, turned blue and then green by addition of stannous chloride. It is obtained by reducing *o*-nitrophenol and is used for dyeing furs. Its methyl ether, *o-anisidine*, $NH_2 \cdot C_6H_4 \cdot OCH_3$, prepared by reducing *o*-nitroanisole, is used in the preparation of synthetic guaiacol (see p. 644), and hence of synthetic vanillin (*see later*), and of various important azo dyes (fast chrome yellow G^1G^2, azoeosin, azocochineal, diazo-scarlet).

m-Aminophenol, m.-pt. 122°, is prepared by heating resorcinol, aqueous ammonia and ammonium chloride under pressure and is used for making dyes. The corresponding dimethyl- and diethyl-amino compounds serve for making rhodamines.

p-Aminophenol, m.-pt. 184°, is readily oxidisable, and is prepared by reducing *p*-nitrophenol, or by the electrolytic reduction of nitrobenzene. It is used for making various

dyes, for dyeing hair and furs, and as a photographic developer under the name *rodinal* (*see* Vol. I., p. 714).[1]

p-Methylaminophenol Sulphate, $OH \cdot C_6H_4 \cdot NH \cdot CH_3, \frac{1}{2}H_2SO_4$, is largely used as a developer under the name *metol*, and is prepared from quinol and methylamine under pressure ; it melts at 250° to 260°.

AMINOANISOLES (Anisidines), $NH_2 \cdot C_6H_4 \cdot OCH_3$, and Phenetidines, $NH_2 \cdot C_6H_4 \cdot OC_2H_5$, are used in making azo-dyes and are similar to aniline. Glacial acetic acid yields, for example, *phenacetin* (*Acetyl-p-phenetidine*), $CH_3 \cdot CO \cdot NH \cdot C_6H_4 \cdot OC_2H_5$, phenetole being $C_6H_5 \cdot OC_2H_5$. Phenacetin is used as an antipyretic and antineuralgic and forms colourless and tasteless white crystals, m.-pt. 135°, which are soluble in alcohol and slightly so in water.

p-PHENETIDINE (ethyl ether of *p*-aminophenol) is used in making various dyes (*stable acid blue*, *alizarin yellow* 5G, etc.), and its hydrochloride, when heated with urea, forms *dulcin* (*sucrol*), $C_2H_5O \cdot C_6H_4 \cdot NH \cdot CO \cdot NH_2$, m.-pt. 173°, which is 200 times as sweet as sugar (saccharin is 500 times as sweet). Phenetidine is used also in pharmacy.

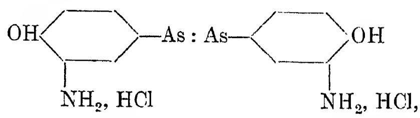
PHENACETIN (*see above*), in doses of 0·5 grm., is an excellent antipyretic and a specific antineuralgic, causing no disturbance in the system. It melts at 135° and is obtained by heating together *p*-phenetidine and acetic acid. In its manufacture use is found for the *p*-nitrophenol obtained in large quantities as a waste product in making blue azo dyes.

2 : 4-DIAMINOPHENOL is used as a photographic developer as sulphate (*amidol*) or hydrochloride (*diamol*), and is employed also for dyeing hair and furs deep chestnut.

DIHYDROXYDIAMINOARSENOBENZENE is the product prepared by Ehrlich and Bertheim as hydrochloride and placed on the market in 1910 under the name *salvarsan* or 606. It is a straw-yellow powder, dissolving in water to an acid solution, and it contains 34 per cent. of arsenic. It also bears the name *Hata*, since it was Dr. Hata, of the Ehrlich Institute, who first injected it into animals and found it to be highly efficacious in cases of syphilis in rabbits, which were able to withstand a certain dose of the preparation. It was applied to man by Alt in the case of a syphilitic paralytic, and was subsequently largely used with success by Iversen.

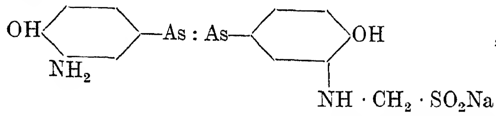
Salvarsan is a specific remedy for syphilis, the spirochetes being killed in 24 to 48 hours and the syphilitic symptoms disappearing rapidly even where treatment with mercury or iodine is without effect. The cure seems, however, to be very painful, relapse and secondary effects sometimes occurring. The firm of Meister, Lucius und Brüning (Höchst, near Frankfort), who make salvarsan, sold a million pounds' worth of it in 1911.

Salvarsan has the constitution :



so that it is $p : p'$-dihydroxy-$m : m'$-diaminoarsenobenzene dihydrochloride.

Salvarsan cannot be injected as such into the veins, but must first be transformed into the sodium salt, the two phenolic hydroxyl groups being salified. The solution for injection should be prepared a few instants before use in order to avoid the formation of the highly poisonous salvarsan oxide. *Neosalvarsan*,



, $2H_2O$,

is more resistant to oxidation, but may deposit the base of 606, which the feeble alkalinity of the blood may be unable to dissolve ; to avoid this inconvenience neosalvarsan may be mixed with various salts (neosalvarsan, 1914) which, however, lower the arsenic content from 30·6 to 20 to 21 per cent.

Besides being used for curing syphilis (90 per cent. of cures). salvarsan is administered also in cases of sleeping sickness, tertiary malaria, etc.

THIOPHENOL (Phenyl hydrosulphide), $C_6H_5 \cdot SH$, is obtained by heating phenol with

[1] Aromatic *photographic developers* should contain several hydroxyl- or amino-groups, or at least one group of each kind ; if the hydrogen of the hydroxyl- and amino-groups is partly replaced, the compounds lose their developing properties, unless some of these groups remain unchanged.

phosphorus pentasulphide or by reducing benzenesulphonic chloride, $C_6H_5 \cdot SO_2Cl$. It is a liquid of very unpleasant odour and exhibits the characters of the mercaptans.

It readily forms salts, that of mercury, $(C_6H_5S)_2Hg$, for example, crystallising in needles. When oxidised in ammoniacal solution, thiophenol yields **Phenyl disulphide**, $(C_6H_5)_2S$, melting at 60°.

Phenyl sulphide, $(C_6H_5)_2S$, is obtained from thiophenol and diazobenzene chloride, and has an alliaceous odour.

AMINOTHIOPHENOLS, $NH_2 \cdot C_6H_4 \cdot SH$. The ortho-compound readily forms condensation products of the type $C_6H_4\left\langle \begin{matrix} N \\ S \end{matrix} \right\rangle CH$, or of greater complexity, such as *primuline* (a yellow dye diazotised on the fibre), which is obtained by heating *p*-toluidine with sulphur and then sulphonating. When heated with sodium sulphide and sulphur, *p*-aminophenol yields *Vidal black*, which colours cotton in an alkaline and reducing bath of sodium sulphide. The black thus obtained is brilliant and stable, like most of these *sulphur dyes*.

PHENOLSULPHONIC ACIDS, $OH \cdot C_6H_4 \cdot SO_3H$, are obtained from phenol and concentrated sulphuric acid or, better, from benzenesulphonic acid. The ortho- and para-compounds are preferably formed, and the former is transformed into the latter on heating. The meta-derivative is prepared indirectly. The ortho-compound is used as an antiseptic under the name *sozolic acid* or *aseptol*.

I. AZO-, DIAZO-, AND DIAZOAMINO-COMPOUNDS AND HYDRAZINES

1. AZO-DERIVATIVES

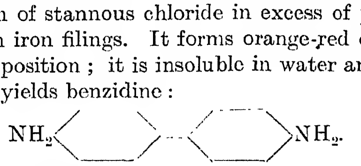
These are intermediate reduction products of nitro-compounds and contain a characteristic group of two nitrogen atoms, each of which is united to an aromatic group.

In acid solution hydrogen reduces nitro-derivatives directly to aromatic amines, but in *alkaline* solution two benzene nuclei condense and become joined by two nitrogen atoms. In this way the following compounds can be obtained from nitrobenzene: (1) **Azoxybenzene**, $C_6H_5 \cdot N : \underset{\underset{O}{\|}}{N} \cdot C_6H_5$; (2) **Azobenzene**, $C_6H_5 \cdot N : N \cdot C_6H_5$; (3) **Hydrazobenzene**, $C_6H_5 \cdot NH \cdot NH \cdot C_6H_5$. Reduction of nitrobenzene with zinc dust in neutral solution yields **Phenylhydroxylamine**, $C_6H_5 \cdot NH \cdot OH$.

When aliphatic amines are oxidised, the alkyl groups are detached in the form of acids and ammonia is generated, but the aromatic amines yield important intermediate compounds, *e.g.*, azoxy-derivatives.

Azo-compounds are crystalline, indifferent, more or less yellowish red compounds. They are soluble in alcohol, but insoluble in water, and some of them distil unchanged. Halogens replace the hydrogen in their aromatic nucleus, oxidising agents convert them into azoxy-compounds, and reducing agents into hydrazo- and amino-compounds. They are obtained, together with azoxy-compounds, also by oxidising amines with permanganate: $2C_6H_5 \cdot NH_2 + O_2 = C_6H_5 \cdot N : N \cdot C_6H_5 + 2H_2O$.

AZOBENZENE (**Benzeneazobenzene**), $C_6H_5 \cdot N : N \cdot C_6H_5$, is obtained by reducing nitrobenzene with a solution of stannous chloride in excess of potassium hydroxide or by distilling azoxybenzene with iron filings. It forms orange-red crystals melting at 68° and boils at 293° without decomposition; it is insoluble in water and is volatile in steam. On reduction in acid solution it yields benzidine:



Higher homologues, such as **Azotoluene**, are also known.

Azoxy-derivatives are neutral compounds obtained by reducing the corresponding nitro-compounds with alcoholic sodium hydroxide or by oxidising azo-compounds by means of hydrogen peroxide.

AZOXYBENZENE is formed by oxidising aniline with potassium permanganate in

alkaline solution or, better, by boiling nitrobenzene with alcoholic potash. It forms pale yellow crystals melting at 36°. When heated with concentrated sulphuric acid, it is converted into **HYDROXYAZOBENZENE**:

$$C_6H_5 \cdot \underset{\diagdown O \diagup}{N - N} \cdot C_6H_5 \rightarrow C_6H_5 \cdot N : N \cdot C_6H_4 \cdot OH.$$

Hydroxyazo-compounds are formed also by the action of diazo-compounds on phenols (especially resorcinol and the naphthols) in presence of alkali:

$$C_6H_5 \cdot N_2 \cdot Cl + C_6H_5 \cdot OK = C_6H_5 \cdot N : N \cdot C_6H_4 \cdot OH + KCl.$$

These compounds form yellow, red, or brown crystals, readily soluble in alcohol but insoluble in water. They are azo-dyes (*tropæolines*).

AMINOAZOBENZENES are obtained by the following methods, which introduce the amino-group into the para-position: *Aminoazobenzene* itself is formed by nitrating azobenzene and reducing the mononitroazobenzene thus obtained; or by transposition of the diazoamino-compounds (*see* p. 672), and hence indirectly from diazobenzene and a primary or secondary amine; or by *coupling* diazo-compounds with tertiary amines, in which case the aminic hydrogen of the aminoazo-compounds is substituted. If the aminic group cannot enter the para-position, owing to this being occupied, the reaction becomes more difficult and *o*-aminoazo-derivatives are formed. The interaction of diazo-compounds with *m*-diamines yields *diaminoazobenzenes*, which are yellow, red, or brown dyes and are termed **Chrysoidines**, $C_6H_5 \cdot N_2 \cdot Cl + C_6H_4(NH_2)_2 = HCl + C_6H_5 \cdot N : N \cdot C_6H_3(NH_2)_2$ (chrysoidine). The amino-group of *p*-aminoazobenzenes can also be diazotised, giving diazo-compounds, which again react with amines to form a group of substances called *bisazo-compounds* or *tetrazo-compounds*, *e.g.*, $C_6H_5 \cdot N : N \cdot C_6H_4 \cdot N : N \cdot C_6H_4 \cdot NH_2$; trisazo-compounds are also known. These substances are used for making *Biebrich scarlet*, croceine, etc.

p-**Aminoazobenzene**, or aniline yellow, $C_6H_5 \cdot N : N \cdot C_6H_4 \cdot NH_2$, forms yellow needles or scales, m.-pt. 127°, b.-pt. 225° at 12 mm. pressure; it boils without decomposition also at the ordinary pressure. It dyes woollen fabrics yellow but the colour is not fast as it slowly sublimes; it is used as *alcohol yellow* to dye lacs, fats, butter, cheese, etc. It forms two hydrochlorides, the yellow having possibly the quinonoid form, $C_6H_5 \cdot NH \cdot N : C_6H_4 : NH_2Cl$, and the flesh-red the structure, $C_6H_5 \cdot N : N \cdot C_6H_4 \cdot NH_2, HCl$. It is used in making many diazo colouring matters, *acid yellow* or *stable yellow* (mono- and di-sulphonic acids as sodium salts), *p*-phenylenediamine, indulines, etc.

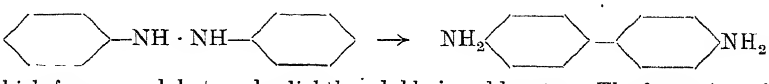
Di- and tri-aminoazobenzenes and **aminoazotoluenes** are also known.

Dimethylaminoazobenzene, $C_6H_5 \cdot N : N \cdot C_6H_4 \cdot N(CH_3)_2$, obtained by coupling diazobenzene chloride with dimethylaniline, forms yellow scales, m.-pt. 117°, and its hydrochloride, violet needles; it is used for colouring butter. The sodium salt of its monosulphonic derivative, $SO_3Na \cdot C_6H_4 \cdot N : N \cdot C_6H_4 \cdot N(CH_3)_2$, is the indicator *methyl orange* (or *tropæoline II.* or *orange III.*), which is insensitive to carbonic acid and to hydrogen sulphide.

HYDRAZO-DERIVATIVES are colourless, crystalline substances of neutral reaction which are decomposed on boiling; hydrazobenzene, for instance, gives aniline and azobenzene. They are obtained by reducing azo-compounds with ammonium sulphide or sodium hydrosulphite, or zinc dust and alkali. Oxidising agents (*e.g.*, $FeCl_3$ or, slowly, the air) convert them into azo-compounds; energetic reducing agents, such as sodium amalgam, give amino-compounds. Strong acids produce molecular transpositions (especially if the para-position to the NH group is free) with formation of diaminodiphenyl compounds, hydrazobenzene giving benzidine (*see below*).

HYDRAZOBENZENE, $C_6H_5 \cdot NH \cdot NH \cdot C_6H_5$, is obtained by reducing azobenzene or nitrobenzene with zinc dust and alcoholic potash, and forms colourless crystals melting at 131°. With energetic reducing agents it gives aniline, while oxidising agents ($FeCl_3$ or atmospheric oxygen) convert it into azobenzene.

Under the action of a strong acid it undergoes transformation, even in the cold, into **Benzidine** (*diaminodiphenyl*):


(*benzidine*)

which forms a sulphate only slightly soluble in cold water. The formation of benzidine in this way shows that it contains the amino-groups in the para-positions, and this is con-

firmed by the fact that this transformation does not occur with a hydrazobenzene in which the para-hydrogen is replaced by another group.

Electrolytic Reduction of Nitro-derivatives. This has been studied more especially by Gattermann, Haber and Elbs, who found that, in the electrolytic conversion of nitrobenzene to aniline in acid solution, various intermediate products are formed, the *primary* ones being :

$$\underset{\text{Nitrobenzene}}{C_6H_5\cdot NO_2} \longrightarrow \underset{\text{Nitrosobenzene}}{C_6H_5\cdot NO} \longrightarrow \underset{\text{Phenylhydroxylamine}}{C_6H_5\cdot NH\cdot OH} \longrightarrow \underset{\text{Aniline}}{C_6H_5\cdot NH_2},$$

whilst in *alkaline* alcoholic solution two secondary reactions occur, the nitrosobenzene first formed reacting with the phenylhydroxylamine formed later, giving azoxybenzene :

$$C_6H_5\cdot NH\cdot OH + C_6H_5\cdot NO = H_2O + C_6H_5\cdot \underset{\diagdown O \diagup}{N - N}\cdot C_6H_5,$$

this being subsequently reduced to hydrazobenzene, which reacts with the excess of nitrobenzene, forming azobenzene and azoxybenzene.

The reduction of hydrazobenzene to aniline requires a tension at the cathode much greater than suffices for the formation of nitrosobenzene and phenylhydroxylamine ; with 1·47 volts, only traces of aniline are formed.

2. DIAZO-DERIVATIVES

In the diazo-compounds of the aromatic series (discovered by P. Griess in 1859) the characteristic group, — N_2 —, is united to only one aromatic radical (*aryl*, *Ar*) and to an acid residue (X). This group therefore forms two series of compounds.

(1) *Diazonium* salts, in which one atom of nitrogen is pentavalent as in ammonium salts. Hantzsch showed their structure to be : $Ar\cdot \underset{\underset{X}{|}}{N} \vdots N$.

(2) True *diazo-compounds* with two trivalent nitrogen atoms, $Ar\cdot N : N\cdot X$; these exist in two stereoisomeric forms (*see* p. 22), the somewhat unstable *syn-diazo*-compounds, $\begin{array}{r}Ar\cdot N\\ \| \\ X\cdot N\end{array}$, and the stable *anti-diazo*-compounds, $\begin{array}{l}Ar\cdot N\\ \quad\ \| \\ \quad\ N\cdot X\end{array}$.

The two groups Ar and X are far apart in the *anti*-compounds, so that they cannot easily react, these compounds hence being the more stable. The cyanide of *antidiazo-p-chlorobenzene*, $\begin{array}{l}Cl\cdot C_6H_4\cdot N\\ \qquad\qquad\ \| \\ \qquad\qquad\ N\cdot CN\end{array}$, is not decomposed by powdered copper and, on the other hand, cannot have the constitution of a diazonium salt, $Cl\cdot C_6H_4\cdot \underset{\underset{CN}{|}}{N} \vdots N$, which, like ammonium salts, should be colourless (whereas the cyanide is yellow) and should have an alkaline reaction and conduct the electric current in aqueous solution ; neither of these properties is shown by this cyanide, although they are found with the analogous *diazoanisole* cyanide, $CH_3O\cdot C_6H_6\cdot \underset{\underset{CN}{|}}{N} \vdots N$.

The *antidiazotates* behave partly like acids and the corresponding *pseudo-acids*. Indeed, antidiazo-hydrate gives the reaction for hydroxyl and forms a conducting aqueous solution ; it is unstable and is converted by acids into the *nitrosamine* (pseudo-acid), which no longer gives the reactions for hydroxyl, does not conduct, has a neutral reaction, and in dry ethereal solution does not form the ammonium salt with ammonia (as, for example, **Phenylnitromethane** does). By alkali the nitrosamine is immediately reconverted into the antidiazotate :

$$\underset{\text{Nitrosamine}}{\begin{array}{l} Ar \cdot N \cdot H \\ \quad | \\ \quad N : O \end{array}} \longrightarrow \underset{\text{Antidiazotate}}{\begin{array}{l} Ar \cdot N \\ \quad \| \\ \quad N \cdot OH \end{array}}$$

PREPARATION. The gradual addition of sodium nitrite (1 grm.-mol.) solution to a solution of the salt of the amine (1 grm.-mol.) cooled with ice results in the formation of the soluble diazonium salt:

$$\underset{\text{Aniline nitrate}}{C_6H_5 \cdot NH_2, HNO_3} + NO \cdot OH = 2H_2O + \underset{\text{Phenyldiazonium nitrate}}{C_6H_5 \cdot N_2 \cdot NO_3}.$$

$$\underset{\text{Aniline hydrochloride}}{C_6H_5 \cdot NH_2, HCl} + NO \cdot OH = 2H_2O + \underset{\text{Phenyldiazonium chloride}}{C_6H_5 \cdot N_2 \cdot Cl}.$$

When aliphatic amines are treated with nitrous acid, nitrogen is evolved, and a primary alcohol formed: $C_2H_5 \cdot NH_2 + NO \cdot OH = N_2 + H_2O + C_2H_5 \cdot OH$.

These diazonium salts are highly explosive when dry, so that they are always used in aqueous solution, when they are completely harmless.

In these compounds the group $C_6H_5 \cdot N_2 \cdot$ behaves like the ammonium cation and with strong mineral acids gives neutral salts, while the salts formed with carbonic acid have alkaline reactions, since, like the alkaline carbonates (*see* Vol. I., pp. 271 and 546), they readily undergo hydrolytic dissociation.

These salts have extremely high conductivities, and hence are dissociated like potassium and ammonium chlorides, and like these, too, they form *diazonium platinichloride*, $(C_6H_5 \cdot N_2 \cdot Cl)_2PtCl_4$. The hydroxide, $C_6H_5 \cdot N_2 \cdot OH$ (from the chloride + AgOH), is known, although it has not yet been isolated; it is soluble, colourless, and strongly alkaline. All these reactions indicate the existence of a pentavalent nitrogen atom in the group N_2. Two constitutional formulæ are hence possible: $C_6H_5 \cdot N \vdots NX$ and $\begin{array}{l} C_6H_5 \cdot N : N \\ \qquad | \\ \qquad X \end{array}$; various reactions indicate the latter to be the more probable (*see above*).

PROPERTIES. There are various ways of eliminating the nitrogen from diazo-compounds in the free state, union taking place between the benzene nucleus and the other group joined to the N_2 complex:

(*a*) By heating the aqueous solution of a diazonium salt a phenol is formed: $C_6H_5 \cdot N_2 \cdot Cl + H_2O = C_6H_5 \cdot OH + N_2 + HCl$.

(*b*) When a diazonium salt is heated with alcohol the benzene nucleus unites with the alkoxy-group:

$$C_6H_5 \cdot N_2 \cdot HSO_4 + C_2H_5 \cdot OH = C_6H_5 \cdot O \cdot C_2H_5 + N_2 + H_2SO_4;$$

under certain conditions, however, the alcohol is oxidised and aldehyde liberated along with the nitrogen:

$$\underset{p\text{-Nitrodiazobenzene chloride}}{NO_2 \cdot C_6H_4 \cdot N_2 \cdot Cl} + C_2H_5 \cdot OH = C_6H_5 \cdot NO_2 + N_2 + HCl + \underset{\text{Acetaldehyde}}{CH_3 \cdot CHO}.$$

(*c*) When a diazonium chloride is treated with either cuprous chloride dissolved in concentrated hydrochloric acid (Sandmeyer) or finely divided copper (Gattermann), the chlorine (or other halogen) is introduced into the nucleus: $C_6H_5 \cdot N_2Cl = C_6H_5 \cdot Cl + N_2$, or $C_6H_5 \cdot N_2Cl + CuBr = CuCl + N_2 + C_6H_5Br$. Azo-derivatives may, however, also be formed: $2C_6H_5N_2Cl + 2CuCl = 2CuCl_2 + C_6H_5 \cdot N_2 \cdot C_6H_5 + N_2$.[1]

[1] Contardi (1922) found that in many reactions, especially with more or less halogenated anilines, cupric salts give results as good as, or even better than, cuprous salts, the formation of

(*d*) Hydriodic acid, potassium iodide, and hydrogen sulphide often act in an analogous manner, whilst by means of cuprous cyanide it is possible to replace an amino group by a cyanogen group by passing through the diazo-compound :

$$C_6H_5 \cdot N_2Cl + KCN = KCl + N_2 + \underset{\text{Benzonitrile}}{C_6H_5 \cdot CN}.$$

This is a general reaction for obtaining (by subsequent hydrolysis) *aromatic acids*.

(*e*) Dry diazobenzene chloride, when treated with benzene in presence of aluminium chloride, gives *diphenyl* :

$$C_6H_5N_2Cl + C_6H_6 = N_2 + HCl + C_6H_5 \cdot C_6H_5.$$

(*f*) Treatment of a diazo-compound with a primary or secondary amine (or treatment of the amine with nitrous acid without other acid) yields *diazoamino-compounds* (*see later*), which are then easily converted into aminoazo-compounds.

With tertiary amines, diazonium salts condense in the para-position, giving *aminoazo-derivatives* :

$$C_6H_5N_2Cl + C_6H_5N(CH_3)_2 = HCl + C_6H_5 \cdot N : N \cdot C_6H_4(CH_3)_2.$$

Diazonium salts also form hydroxyazobenzenes (*see* p. 668).

DIAZOBENZENE CHLORIDE (**Phenyldiazonium chloride**), $C_6H_5 \cdot N_2 \cdot Cl$, forms colourless needles soluble in water and is obtained by the action of moist AgCl on the corresponding bromide ; the *bromide* is obtained in nacreous scales by the interaction of ethereal solutions of bromine and diazoaminobenzene (tribromoaniline remains in the solution). In solution, as usually employed, it is obtained by diazotising aniline hydrochloride.

DIAZOBENZENE NITRATE (**Phenyldiazonium nitrate**), $C_6H_5 \cdot N_2 \cdot NO_3$, is the salt which is most widely used, and is obtained by passing nitroso-nitric fumes into a cold ethereal solution of diazoaminobenzene or into an aqueous paste of aniline nitrate until this is dissolved ; to the filtered liquid are added the triple volume of alcohol and then ether until the nitrate separates in colourless needles. It is readily soluble in water but insoluble in ether, benzene, chloroform, etc. It has a strong acid reaction and is easily exploded by shock.

DIAZOBENZENE SULPHATE (**Phenyldiazonium sulphate**), $C_6H_5 \cdot N_2 \cdot HSO_4$, is best obtained by treating a concentrated solution of crude diazobenzene nitrate with moderately concentrated sulphuric acid, precipitating several times with excess of alcohol and with ether, and allowing to crystallise in a desiccator. It forms crystals which are readily soluble in water and deflagrate at 100°.

DIAZOBENZENE PERBROMIDE, $C_6H_5 \cdot N_2 \cdot Br_3$, is prepared by the action of hydrobromic acid and bromine water on diazobenzene salts, and when treated with ammonia gives **DIAZOBENZENEIMIDE** (**Benzeneazimide**), $C_6H_5N_2Br_3 + NH_3 = 3HBr + C_6H_5 \cdot N\Big\langle\begin{matrix}N\\ \|\\ N\end{matrix}$; this is more easily obtained by the action of nitrous acid on phenylhydrazine and may be regarded as the phenyl derivative of azoimide (Vol. I., p. 376).

DIAZOBENZENESULPHONIC ACID, $C_6H_4\Big\langle\begin{matrix}N_2 \cdot OH\\ \\ SO_3H\end{matrix}$, is known as the anhydride $C_6H_4\Big\langle\begin{matrix}N_2\\ |\\ SO_3\end{matrix}$, and is obtained by adding a mixture of sodium sulphanilate and sodium

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azo-compounds being then impossible. For cupric salts the interpretation given by Hantzsch for cuprous salts holds :

$$\underset{Cl}{C_6H_5 \cdot N} : N + CuCl_2 = \underset{Cl}{C_6H_5 \cdot N} : NCl \cdot CuCl \longrightarrow CuCl_2 + C_6H_5 \cdot N : NCl \longrightarrow C_6H_5Cl + N : N.$$

Some nitrohalogenated amines, after conversion into diazonium salts, undergo further nitration in the nucleus when treated with sodium nitrite in acid solution ; thus, with 2 : 6-dichloro-4-nitroaniline :

$$NO_2 \cdot C_6H_2Cl_2 \cdot N(NO_3) : N \longrightarrow NO_2 \cdot C_6H_2Cl_2 \cdot N(NO_3) : NH \cdot NO_2 \longrightarrow NO_2 \cdot C_6H_2Cl_2 \cdot N : N \cdot NO_2 \longrightarrow NO_2 \cdot C_6H_2Cl_2 \cdot NO_2.$$

nitrite to dilute sulphuric acid. It forms white needles readily soluble in water, and is used to prepare azo dyes.

With KOH, *phenyldiazonium hydroxide* forms a potassium compound, $C_6H_5 : N_2 \cdot OK$, and hence behaves as an acid besides as a base, but as it cannot be assumed that these two functions are exhibited to such marked extents by one and the same substance, Hantzsch supposes that, in aqueous solution, it forms a mixture of *phenyldiazonium hydroxide*, $\begin{matrix} C_6H_5 \cdot N \cdot OH, \\ \vert\vert\vert \\ N \end{matrix}$ and *syn-diazobenzene hydroxide*, $C_6H_5 \cdot N : N \cdot OH$, so that the general reactions mentioned above would be explained thus:

$$\begin{matrix} C_6H_5 \cdot N \vdots N \\ \vert \\ Cl \end{matrix} + H \cdot OH = HCl + C_6H_5 \cdot N : N \cdot OH \longrightarrow C_6H_5 \cdot OH + N \vdots N.$$

None of the reactions referred to above can be explained well without assuming the passage of *diazonium* salts with pentavalent nitrogen into true diazo-compounds with trivalent nitrogen ($- N = N -$) (*see above*).

3. DIAZOAMINO-DERIVATIVES

These contain the aminodiazo-group, $- N = N - NH -$, and are yellow, crystalline substances which do not combine with acids. They are obtained by adding to diazo-salts (freshly formed in solution) primary or secondary amines, *e.g.*, aniline hydrochloride; the separation of the yellow crystalline mass is hastened by addition of concentrated sodium acetate solution:

$$C_6H_5 \cdot N_2 \cdot Cl + C_6H_5 \cdot NH_2 = HCl + C_6H_5 \cdot N_2 \cdot NHC_6H_5.$$

To 2 mols. of aniline and 3 mols. of hydrochloric acid, kept cool with ice, is slowly added 1 mol. of sodium nitrite, the liquid being then precipitated with concentrated sodium acetate solution.

They are also formed directly from free aniline and nitrous acid, in which case diazobenzene hydroxide must be regarded as an intermediate product:

$$(a)\ C_6H_5 \cdot NH_2 + HNO_2 = H_2O + C_6H_5 \cdot N_2 \cdot OH;$$
$$(b)\ C_6H_5 \cdot N_2 \cdot OH + C_6H_5 \cdot NH_2 = H_2O + C_6H_5 \cdot N_2 \cdot NHC_6H_5.$$

With nitrous acid in acid solution, diazoamino-compounds are converted into diazonium salts, the remaining aminic residue, $- NHC_6H_5$, being diazotised:

$$C_6H_5 \cdot N : N \cdot NHC_6H_5 + HNO_2 + 2HCl = 2H_2O + 2C_6H_5 \cdot N_2Cl.$$

When heated with aniline hydrochloride, diazoaminobenzene solution yields aminoazobenzene, which is a colouring matter from which others are derived. In this transformation, which is common to all diazoamino-compounds, the aniline hydrochloride acts catalytically and takes no part in the reaction; the amino-group is carried to the para-position with respect to the diazo group, or, if this is occupied, to the ortho-position:

$$\underset{\text{Diazoaminobenzene}}{C_6H_5 \cdot N : N \cdot NHC_6H_5} \longrightarrow \underset{\text{Aminoazobenzene}}{C_6H_5 \cdot N : N \cdot C_6H_4 \cdot NH_2}.$$

It has been shown by H. Goldschmidt that the velocity constant of this transformation increases with the amount of the catalyst (aniline hydrochloride), and the catalytic powers of the different amine salts are proportional to their degrees of dissociation in water.

4. HYDRAZINES

These compounds are obtained by reducing diazonium salts with a hydrochloric acid solution of stannous chloride:

$$C_6H_5N_2Cl + 4H = \underset{\text{Phenylhydrazine hydrochloride}}{C_6H_5 \cdot NH \cdot NH_2, HCl}.$$

The use of sodium sulphite in place of stannous chloride gives first the diazosulphonate, which, when treated with zinc dust and acetic acid and subsequently boiled with hydrochloric acid, gives phenylhydrazine hydrochloride; this salt separates out, being only slightly soluble in water and less so in acid.

The three stages of the reaction are as follow:

$$(a)\ \underset{\text{Diazobenzene chloride}}{C_6H_5N_2Cl} + Na_2SO_3 = \underset{\text{Sodium diazobenzenesulphonate}}{C_6H_5 \cdot N_2 \cdot SO_3Na} + NaCl.$$

$$(b)\ C_6H_5 \cdot N_2 \cdot SO_3Na + 2H = \underset{\text{Sodium phenylhydrazinesulphonate}}{C_6H_5 \cdot NH \cdot NH \cdot SO_3Na}.$$

$$(c)\ C_6H_5 \cdot NH \cdot NH \cdot SO_3Na + H_2O = NaHSO_4 + \underset{\text{Phenylhydrazine}}{C_6H_5 \cdot NH \cdot NH_2}.$$

PHENYLHYDRAZINE, $C_6H_5 \cdot NH \cdot NH_2$, is the most important member of this group and has a basic character, forming well-crystallised salts. It is a colourless, oily liquid which turns brown in the air; it dissolves only slightly in water, melts at 19·6°, and boils at 243° with slight decomposition; it distils unchanged in a current of steam. With energetic reducing agents it forms aniline and ammonia, and with oxidising agents (*e.g.*, chloride of lime) it can form diazonium compounds, but usually nitrogen is eliminated with formation of water and benzene. It gives characteristic reactions with *lactones, sugars, aldehydes,* and *ketones* (*see* pp. 246 and 253), and reduces Fehling's solution in the cold.

With diketones it forms *phenylosazones* (*see* p. 524), and with acetoacetic acid it forms phenylmethylpyrazolone, from which, by methylation, *antipyrine* is obtained. With nitrous acid phenylhydrazine gives the highly poisonous *nitrosophenylhydrazine*, $C_6H_5 \cdot N(NO) \cdot NH_2$.

The constitution of phenylhydrazine is proved by the fact that nitrosomethylaniline, $C_6H_5 \cdot N(CH_3) \cdot NO$ (obtained from the secondary amine, methylaniline, $C_6H_5 \cdot NH \cdot CH_3$, by the action of nitrous acid), on reduction, yields *as-phenylmethylhydrazine*, $C_6N_5 \cdot N(CH_3) \cdot NH_2$, which can also be obtained from phenylhydrazine by the action of metallic sodium (this replaces the iminic hydrogen) and subsequently of methyl iodide:

$$C_6H_5 \cdot NH \cdot NH_2 \longrightarrow C_6H_5 \cdot \underset{\substack{|\\ Na}}{N} \cdot NH_2 \longrightarrow C_6H_5 \cdot \underset{\substack{|\\ CH_3}}{N} \cdot NH_2.$$

Replacement of the aminic hydrogen by an acid residue yields *hydrazides* (α and β), which give a reddish violet coloration with sulphuric acid and potassium dichromate. The hydrazides are insoluble in water and may hence be used for the precipitation of soluble acids.

DIPHENYLHYDRAZINE, $(C_6N_5)_2N \cdot NH_2$, is obtained by reducing **diphenylnitrosamine**, $(C_6H_5)_2N \cdot NO$, in alkaline solution with zinc dust and acetic acid. It is a base boiling at 34° almost without decomposition, and oxidising readily in the air; its salts are unstable. It is insoluble in water and hence reduces Fehling's solution only slightly, even in the hot. With concentrated sulphuric acid it gives a blue coloration. The action of oxidising agents distinguishes it from the isomeric hydrazobenzene; the latter gives azobenzene, whilst diphenylhydrazine yields in the cold **tetraphenyltetrazone**, $(C_6H_5)_2N \cdot N : N \cdot N(C_6H_5)_2$, and in the hot diphenylamine and violet colouring-matters with abundant evolution of nitrogen. With nitrous acid, hydrazobenzene forms nitroso-derivatives, whilst diphenylhydrazine, like other secondary hydrazines, gives diphenylnitrosamine and nitrous oxide.

BENZYLPHENYLHYDRAZINE, $C_6H_5 \cdot CH_2 \cdot N(C_6H_5) \cdot NH_2$, is obtained from phenylhydrazine and benzyl chloride. **Benzylhydrazine**, $C_6H_5 \cdot CH_2 \cdot NH \cdot NH_2$, boiling at 135° (*in vacuo*), is also known.

p-**NITROPHENYLHYDRAZINE**, obtained from *p*-nitraniline, forms yellow crystals and is a useful reagent for aldehydes and ketones.

β-**PHENYLHYDROXYLAMINE**, $C_6H_5 \cdot NH \cdot OH$, is obtained by the gentle oxidation of aniline or the cautious reduction of nitrobenzene with zinc dust and water, and forms colourless crystals melting at 81°. With acids it gives *p*-aminophenol, with oxygen azoxybenzene and with dichromate nitrosobenzene. The α-isomeride, $NH_2 \cdot OC_6H_5$, is of little importance.

J. ROMATIC ALCOHOLS, ALDEHYDES, AND KETONES

In these compounds the primary alcohol group, the aldehyde group, or the ketonic group forms a side-chain to the benzene nucleus and shows all the general properties of these groups. Di- and trihydric alcohols are also known, *e.g.*, **Phthalic alcohol** (ortho); **Xylylene alcohol** (para), $C_6H_4(CH_2 \cdot OH)_2$; **Phenylglycerol**, $C_6H_5 \cdot CH(OH) \cdot CH(OH) \cdot CH_2 \cdot OH$.

BENZYL ALCOHOL, $C_6H_5 \cdot CH_2 \cdot OH$ (discovered by Cannizzaro in 1853), is isomeric with the cresols, $CH_3 \cdot C_6H_4 \cdot OH$, and is obtained by the interaction of benzyl chloride and potassium acetate and subsequent hydrolysis of the acetyl-derivative thus obtained, or, better, by the action of aqueous potassium hydroxide on benzaldehyde:

$$2C_6H_5 \cdot CHO + KOH = C_6H_5 \cdot CO_2K + C_6H_5 \cdot CH_2 \cdot OH.$$

The alcohol readily gives benzyl chloride when treated with PCl_5. On oxidation it gives first benzaldehyde and then benzoic acid, its constitution being thus proved. It forms simple and mixed ethers and esters. It differs from aliphatic alcohols by resinifying with sulphuric acid. It has the characters of a true alcohol and is hence insoluble in alkali (unlike the phenols). It is slightly soluble in alcohol and boils at 206°.

Various higher *homologues* are known: **Tolylene alcohols**, $CH_3 \cdot C_6H_4 \cdot CH_2 \cdot OH$; **Cumyl alcohol** (*p*-), $C_3H_7 \cdot C_6H_4 \cdot CH_2 \cdot OH$, etc.

Styryl alcohol, $C_6H_5 \cdot CH : CH \cdot CH_2 \cdot OH$, containing an unsaturated side-chain, is found as ester (styracin) in storax; it forms acicular crystals with an odour of hyacinth.

With alcoholic potash *aromatic aldehydes* are partly oxidised and partly reduced, benzaldehyde, for instance, being converted into potassium benzoate and benzyl alcohol:

$$2C_6H_5 \cdot CHO + KOH = C_6H_5 \cdot CO_2K + C_6H_5 \cdot CH_2 \cdot OH.$$

With dimethylaniline or phenol these aldehydes give derivatives of **triphenylmethane**:

$$C_6H_5 \cdot CHO + 2C_6H_5 \cdot OH = H_2O + C_6H_5 \cdot CH\begin{cases} C_6H_4 \cdot OH \\ C_6H_4 \cdot OH \end{cases}$$

BENZALDEHYDE, $C_6H_5 \cdot C\begin{cases} O \\ H \end{cases}$, occurs in the **Amygdalin**, $C_{20}H_{27}NO_{11}$, of bitter almonds in the form of a glucoside. It is a liquid of pleasant odour and dissolves slightly in water; it boils at 179°, has the sp. gr. 1·05 and constitutes *bitter almond oil.* When pure it forms crystals, m.-pt. 26°. It oxidises easily and forms crystalline products with bisulphites, while it combines with hydrogen, hydrogen cyanide, etc., forming an oxime, a hydrazone, etc. With ammonia it gives **hydrobenzamide**, $3C_6H_5 \cdot CHO + 2NH_3 = 3H_2O + (C_6H_5 \cdot CH)_3N_2$. It is formed by distilling a mixture of calcium formate and benzoate and also by oxidising benzyl alcohol.

Until recently it was prepared industrially by heating benzylidene chloride under pressure with milk of lime and calcium carbonate:

$$C_6H_5 \cdot CHCl_2 + Ca(OH)_2 = CaCl_2 + C_6H_5 \cdot CHO + H_2O.$$

By using catalysts (finely divided iron, etc.) Schulze found that this reaction could be rendered complete at low temperatures in open vessels, very pure hydrochloric acid being recoverable. Benzaldehyde may also be obtained by treating benzene with a gaseous mixture of carbon monoxide and hydrogen chloride in presence of Cu_2Cl_2 or $AlBr_3$ (Ger. Pat. 126,241).

A method now largely used is that discovered by Poner of the Badische Anilin-und Soda-Fabrik (1887) and kept secret for some years but published in 1898 in the French Patent No. 276,258. It consists in shaking toluene vigorously with sulphuric acid (52° Bé.) and gradually adding precipitated manganese dioxide, the temperature being kept at 40°. The benzaldehyde formed is free from chlorine and may be separated from the toluene by a current of steam, or, better, by diluting the toluene-benzaldehyde mixture with four

times its weight of water and treating the liquid with sulphur dioxide until about 26 per cent. is absorbed. In this way all the aldehyde passes into solution (improvement on the use of sodium bisulphite) and can be decanted from the undissolved toluene. It is then sufficient to heat the sulphurous solution slowly from 30° to 100° to eliminate all the sulphur dioxide, which is passed into a further portion of the aldehyde mixture. After cooling the solution, almost the whole of the benzaldehyde is obtained in a pure state and the mother-liquors are utilised in succeeding operations so that the small amounts of aldehyde remaining dissolved may not be lost.

Commercial benzaldehyde and that for industrial uses cost before the war about 3*s.*, the pure product about 4*s.*, and the chemically pure about 9*s.* 6*d.* per kilo. For industrial purposes, it should have a specific gravity of 1·052 to 1·054, and should distil completely in a current of hydrogen between 176° and 180°. Its solution in concentrated sulphuric acid should be only slightly brown and it should dissolve completely in ammonium bisulphite. Any benzoic acid present can be titrated with phenolphthalein as indicator. It is used mainly as oil of bitter almonds and in perfumery, and also for making dyes of the triphenylmethane series.

HOMOLOGUES OF BENZALDEHYDE are obtained by treating aromatic hydrocarbons with gaseous hydrogen chloride and carbon monoxide in presence of $AlCl_3$ or Cu_2Cl_2. The first product obtained under these conditions is probably formyl chloride, which then reacts thus:

$$X \cdot C_6H_5 + Cl \cdot CHO = HCl + X \cdot C_6H_4 \cdot CHO.$$

Aldehydes are also obtained from ethyl chloroxalate and aromatic hydrocarbons in presence of $AlCl_3$, the ketonic ester obtained being hydrolysed and the acid subjected to dry distillation in order to expel CO_2:

$$X \cdot C_6H_5 + Cl \cdot CO \cdot COOC_2H_5 = HCl + X \cdot C_6H_4 \cdot CO \cdot COOC_2H_5;$$
$$X \cdot C_6H_4 \cdot CO \cdot COOC_2H_5 = X \cdot C_6H_4 \cdot CHO + CO_2$$

The action of HCl and HCN on aromatic hydrocarbons also yields aldehydes, *aldines* being formed as intermediate products:

$$C_6H_6 + HCN + HCl = \underset{\text{Benzaldine hydrochloride}}{C_6H_5 \cdot CH : NH, HCl.}$$

$$C_6H_5 \cdot CH : NH, HCl + H_2O = C_6H_5 \cdot CHO + NH_4Cl.$$

CINNAMALDEHYDE, $C_6H_5 \cdot CH : CH \cdot CHO$, is an oil of pleasant odour, boiling at 246°; it is volatile in steam and is separated from cinnamon oil, of which it is the chief constituent, by means of sodium bisulphite.

NITROBENZALDEHYDES, $NO_2 \cdot C_6H_4 \cdot CHO$, are prepared in various ways. The ortho-compound is obtained either from *o*-nitrobenzyl chloride or by oxidising *o*-nitrotoluene. It forms colourless crystals melting at 46° and with acetone and caustic soda leads to the synthesis of indigo.

Nitration of benzaldehyde yields mainly the *m*-compound, together with 20 per cent. of the *o*-derivative.

CUMINALDEHYDE (Cuminol, Isopropylbenzaldehyde), $C_3H_7 \cdot C_6H_4 \cdot CHO$, occurs in Roman cumin oil.

AROMATIC KETONES

ACETOPHENONE, $C_6H_5 \cdot CO \cdot CH_3$, is obtained by distilling calcium acetate with calcium benzoate or, better, by treating benzene with acetyl chloride in presence of $AlCl_3$.

It forms crystals melting at 20° and boils at 200°; it dissolves only slightly in water, has a pleasant smell, and is used as a hypnotic under the name of **hypnone**. On oxidation it gives either benzylformic acid or benzoic acid and carbon dioxide; halogens give products substituted in the side-chain.

BENZOPHENONE (Diphenyl ketone), $C_6H_5 \cdot CO \cdot C_6H_5$, is obtained either by the dry distillation of calcium benzoate or by the action of benzoyl chloride on benzene in presence of $AlCl_3$. Its behaviour is similar to that of aliphatic compounds, and with hydrogen it forms **Benzhydrol**, $C_6H_5 \cdot CH(OH) \cdot C_6H_5$, and **Benzopinacone**, $(C_6H_5)_2 = \underset{OH}{\underset{|}{C}} - \underset{OH}{\underset{|}{C}} = (C_6H_5)_2$.

When fused with potassium hydroxide, it gives benzene and potassium benzoate :

$$C_6H_5 \cdot CO \cdot C_6H_5 + KOH = C_6H_6 + C_6H_5 \cdot COOK.$$

Benzophenone exists in two modifications which differ physically: an unstable form, m.-pt. 27°, and a stable form, m.-pt. 49°.

DIPHENYLENEKETONE, $\begin{array}{l}C_6H_4\\ |\\ C_6H_4\end{array}\!\!>CO$, is the ketone corresponding with diphenylene-methane (*see later*), and is obtained by heating phenanthraquinone with lime. With nascent hydrogen it gives **Fluorene alcohol,** $\begin{array}{l}C_6H_4\\ |\\ C_6H_4\end{array}\!\!>CH \cdot OH$ (colourless scales, m.-pt. 153°), and, when fused with potash, **Diphenylcarboxylic acid,** $C_6H_5 \cdot C_6H_4 \cdot CO_2H$.

Polyacetones, such as **Benzoylacetone,** $C_6H_5 \cdot CO \cdot CH_2 \cdot CO \cdot CH_3$, and **Acetophenone-acetone,** $C_6H_5 \cdot CO \cdot CH_2 \cdot CH_2 \cdot CO \cdot CH_3$, are also known.

Condensation of benzaldehyde with acetophenone or acetone in presence of NaOH gives unsaturated ketones: **Benzalacetone,** $C_6H_5 \cdot CH : CH \cdot CO \cdot CH_3$ (m.-pt. 41°); **Benzalacetophenone** (*chalkone*), $C_6H_5 \cdot CH : CH \cdot CO \cdot C_6H_5$ (m.-pt. 58°).

AROMATIC OXIMES present interesting cases of isomerism (*see* pp. 22 and 253). Thus, **Benzaldoxime** is known in two forms: liquid *anti-benzaldoxime*, which boils unaltered, and solid *syn-benzaldoxime*, which readily loses water (with acetic anhydride), forming benzonitrile:

$$\begin{array}{c}C_6H_5 \cdot C \cdot H\\ \|\\ N \cdot OH\end{array} = H_2O + C_6H_5 \cdot C \vdots N.$$

Under these conditions the anti-aldoxime gives an acetyl-derivative, so that the two aldoximes may be distinguished in this way.

With *ketoximes* two isomerides are formed *only* when the two groups united to the carbonyl group are different :

$$\begin{array}{c}X - C - X'\\ \|\\ N - OH\\ \textit{syn}\end{array} \quad \text{and} \quad \begin{array}{c}X - C - X'\\ \|\\ OH - N\\ \textit{anti}\end{array}$$

Thus, **Benzophenonoxime,** $\begin{array}{c}C_6H_5 - C - C_6H_5\\ \|\\ N - OH\end{array}$, does not form isomerides, which are, however, obtained if a hydrogen atom of one of the benzene groups is replaced by a halogen, alkyl group, etc.

The *ketoximes* show Beckmann's transposition,[1] in which the isomeric ketoximes, which have different melting-points, give rise to two different substituted amides according as the transposition takes place with the group X or X′ (*see Note*).

[1] The Beckmann transposition is that obtained with ketoximes in general by treating them with acetyl chloride or concentrated sulphuric acid or, in some cases, merely by fusion. The oxygen of the oxime changes places with a radical united to the ketonic carbon giving a substituted amide, an unstable, tautomeric, hydroxyl compound being probably formed as an intermediate product:

$$\begin{array}{c}X \cdot C \cdot X'\\ \|\\ N \cdot OH\end{array} \rightarrow \left[\begin{array}{c}X \cdot C \cdot OH\\ \|\\ N \cdot X'\end{array}\right] \rightarrow \begin{array}{l}X \cdot C : O\\ \;|\\ N{<}^{H}_{X'}\end{array}$$

The structure of the isomeric syn- and anti-oximes can be determined by Beckmann's reaction. Thus, if the above oxime is the anti-compound, the transposition with the syn-isomeride would be as follows:

$$\begin{array}{c}X \cdot C \cdot X'\\ \|\\ OH \cdot N\end{array} \rightarrow \begin{array}{r}O \cdot C \cdot X'\\ |\\ {}^{H}_{X}{>}N\end{array}$$

BENZALAZINE, $C_6H_5 \cdot CH : N \cdot N : CH \cdot C_6H_5$, is obtained by the condensation of 2 mols. of benzaldehyde with 1 mol. of hydrazine (sulphate), and forms yellow crystals melting at 93°.

BENZALDEHYDEPHENYLHYDRAZONE, $C_6H_5 \cdot CH : N \cdot NHC_6H_5$, forms colourless crystals melting at 132° and forms stereoisomerides.

K. AROMATIC HYDROXY-ALCOHOLS, HYDROXY-ALDEHYDES, AND KETONIC ALCOHOLS

$$C_6H_4{<}^{OH}_{CH_2 \cdot OH} \left| \begin{matrix} o \\ m \\ p \end{matrix} \right\} \begin{matrix} \textit{saligenin} \\ \textit{hydroxybenzyl} \\ \textit{alcohols} \end{matrix} \qquad C_6H_4{<}^{OH}_{CHO} \left| \begin{matrix} o \\ m \\ p \end{matrix} \right\} \begin{matrix} \textit{salicylaldehyde} \\ \textit{hydroxybenzalde-} \\ \textit{hydes} \end{matrix}$$

$$C_6H_3 \begin{matrix} OH & 4 \\ OH & 3 \\ CHO & 1 \end{matrix} \ \textit{protocatechualdehyde} \qquad C_6H_4{<}^{OCH_3\ p}_{CH_2 \cdot OH} \ \textit{anisic alcohol} \ \text{(m. pt. 45°; b. pt. 259°)}$$

$$C_6H_4{<}^{OCH_3}_{CHO}\ p \quad \textit{anisaldehyde} \qquad C_6H_3 \begin{matrix} OH & 4 \\ OCH_3 & 3 \\ CH_2 \cdot OH & 1 \end{matrix} \ \textit{vanillic alcohol}$$

$$C_6H_3 \begin{matrix} OH & 4 \\ OCH_3 & 3 \\ CHO & 1 \end{matrix} \quad \textit{vanillin}$$

The three isomeric hydroxybenzyl alcohols are known, their melting points being as follows: *o*-, 82°; *m*-, 67°; *p*-, 110°. The most common of these is:

SALIGENIN (*o*-Hydroxybenzyl alcohol, *see above*), $OH \cdot C_6H_4 \cdot CH_2 \cdot OH$, occurring in the glucoside *salicin*, from which it can be obtained by the action of emulsin, ptyalin or dilute acid (Piria, 1845):

$$C_6H_{11}O_5 \cdot O \cdot C_6H_4 \cdot CH_2 \cdot OH + H_2O = OH \cdot C_6H_4 \cdot CH_2 \cdot OH + C_6H_{12}O_6\ (\textit{glucose}).$$

It is soluble in alcohol, ether, or boiling water and gives a blue coloration with ferric chloride.

AROMATIC HYDROXYALDEHYDES, or phenolic aldehydes, are obtained (1) by the action of chloroform and caustic potash on phenols: $C_6H_5 \cdot OH + 4KOH + CHCl_3 = 3KCl + 3H_2O + CHO \cdot C_6H_4 \cdot OK$; or (2) by the action of hydrocyanic and hydrochloric acids on phenols in presence of aluminium chloride or zinc chloride, *aldim* hydrochlorides being formed as intermediate products.

With difficulty by oxidising agents, but readily by fusion with alkali, these aldehydes give the corresponding hydroxycarboxylic acids. They reduce ammoniacal silver solution but *not Fehling's solution*. With alkali they give soluble alkali phenoxides which form the alkyl derivatives of the phenols when treated with alkyl iodides.

SALICYLALDEHYDE (*o*-Hydroxybenzaldehyde), $OH \cdot C_6H_4 \cdot CHO$, is found in the volatile oil of *Spiraea ulmaria*. Its synthesis by means of chloroform is indicated above and it is separated from the *p*-aldehyde formed at the same time by distillation in steam. It is a liquid, b. pt. 196°, sp. gr. 1·172 at 15°; it dissolves to some extent in water and gives a violet coloration with ferric chloride. Like all *o*-hydroxy aldehydes it colours the skin yellow.

ANISALDEHYDE (*see above*) is obtained by the cautious oxidation of **Anethole**, $CH_3 \cdot CH : CH \cdot C_6H_4 \cdot OCH_3$, with dichromate and sulphuric acid, the aldehyde being distilled in steam and purified by means of sodium bisulphite. It boils at 248°, has sp. gr. 1·123 at 15°, and, owing to its strong odour of hawthorn, is used in perfumery.

VANILLIN, $C_6H_3(OH)(OCH_3)(CHO)$ 4 : 3 : 1 (*m*-Methoxy-*p*-hydroxybenzaldehyde), is found (about 2 per cent.) in the pods or fruit of vanilla (*Vanilla planifolia*) [1] and as a gluco-

[1] Vanilla is a climbing, herbaceous plant growing well in Mexico, Réunion and elsewhere. The fruit is fleshy and cylindrical (15 to 25 cm. long) and contains a number of round black seeds with a pleasant odour. The fruit is gathered before it is quite ripe, as otherwise the pods open and the seeds are lost. Their vitality is destroyed by steeping them in water at 80° to 85° or placing them in an oven at 50° to 70° or in the sunlight. The capsules thus turn dark brown and after being allowed to sweat for 20 to 30 days at 30° to 40° they become covered with a

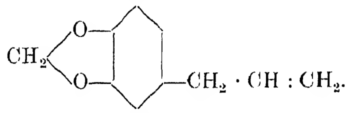
side (coniferin, $C_{16}H_{22}O_8 + 2H_2O$) in the sap of the conifers (*Coniferin*, $C_{16}H_{22}O_8 + 2H_2O$),[1] in asparagus, in beet-juice, in certain woods, in asafœtida, etc.; it is also formed by oxidising the resin of olives.

It is readily obtained artificially by treating clove oil with dilute alkali, which dissolves the eugenol and transforms it into **Isoeugenol**, $C_6H_3(OH)(OCH_3)(CH : CH \cdot CH_3)$, which is then oxidised by ozone or permanganate. It forms slender white crystals which melt at 81° to 81·5°, and sublime, and it boils at 285°. It has a strong odour of vanilla. Considerable quantities of *synthetic vanillin* are now made by various processes, the details of which are kept secret.

By HCl at 200° it is transformed into protocatechu aldehyde, the methylene ether of which constitutes **Piperonal** (*heliotropin* or artificial heliotrope),

$$\begin{array}{l} CH : CH \cdot C \cdot O \diagdown \\ | \qquad\qquad\quad \| \qquad\quad CH_2, \\ CHO \cdot C : CH \cdot C \cdot O \diagup \end{array}$$

(m.-pt. 37°; b.-pt. 263°), costing before the war from 16*s.* to 28*s.* per kilo, according to its purity. Formerly it was obtained by oxidising *piperinic acid* (*see* Piperidine), but it is now made by oxidising *isosafrole*, prepared by the action of alkali on *safrole*,



BENZOYLCARBINOL, $C_6H_5 \cdot CO \cdot CH_2 \cdot OH$, obtained from **Phenacyl bromide**, $C_6H_5 \cdot CO \cdot CH_2Br$, forms stable, shining scales, and possesses strong reducing properties; The corresponding acetonaldehyde is **Phenylglyoxal**, $C_6H_5 \cdot CO \cdot CHO$, analogous to pyruvic aldehyde.

L. AROMATIC ACIDS

Like the aliphatic acids, these form salts, anhydrides, esters, amides, etc., and give in addition other products by substitution in the benzene nucleus.

Here, too, the characteristic group is the carboxyl, COOH, and the acids may be either mono- or poly-basic, according to the number of carboxyl groups, this being indicated in the name:

$C_6H_5 \cdot COOH$	$C_6H_4(COOH)_2$	$C_6H_3(COOH)_3$	$C_6(COOH)_6$
Benzoic acid (benzenecarboxylic or benzenemethanoic acid)	Phthalic acids (benzenedicarboxylic or benzenedimethanoic acids)	Benzenetricarboxylic acids (benzenetrimethanoic acids)	Mellitic acids (benzenehexacarboxylic or benzenehexamethanoic acids)

Aromatic acids with unsaturated side-chains are also known, these behaving like unsaturated aliphatic compounds:

$C_6H_5 \cdot CH : CH \cdot CO_2H$	$C_6H_5 \cdot C : C \cdot CO_2H$
Cinnamic acid	Phenylpropiolic acid

There are also various acids derived from the hydrobenzenes, with characters resembling those of aliphatic compounds.

Aromatic hydroxy-acids with a hydroxyl group in the nucleus behave partly like phenols and partly like acids, and are analogous to the aromatic alcohol-acids containing acid groups and true alcoholic groups in the side-chains.

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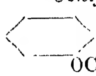
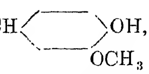
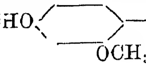
crystalline, perfumed powder. They are then tied up in bundles of 50 and sold in boxes holding 3 to 10 kilos. Of inferior quality are the smaller fruit and those from the Antilles, Brazil, and Guiana. They are used for pastry, liquors, perfumes, and chocolates.

[1] *Coniferin*, m. pt. 185°, is a glucoside of the larch having the constitution $OH \cdot CH_2 \cdot CH : CH$  $O \cdot CH_2 \cdot [CH \cdot OH]_4 \cdot CHO + 2H_2O$. It is lævorotatory and yields glucose and coniferyl alcohol, $OH \cdot CH_2 \cdot CH : CH$  OH, when treated with a dilute acid or emulsin. On reduction it gives eugenol and *glucovanillyl alcohol*, whilst on oxidation it forms first *glucovanillin*, CHO  $O \cdot CH_2 \cdot [CH \cdot OH]_4 \cdot CHO$, which gives vanillin on hydrolysis with dilute acid.

In each of the aliphatic acids a hydrogen atom can be replaced by a benzene residue, giving aromatic acids of the acetic acid series (*e.g.*, **Phenylacetic Acid**, $C_6H_5 \cdot CH_2 \cdot CO_2H$) and of the glycollic and succinic series, etc.

In general, aromatic acids are crystalline and only slightly soluble in water, while they are often soluble in alcohol or ether. The more simple ones sublime or distil unchanged and lose CO_2 only on distillation with soda-lime, this occurring with the more complex acids simply on heating. Their alkaline salts are soluble in water, but the acids are precipitated in the free state on addition of a mineral acid.

GENERAL METHODS OF FORMATION. (*a*) When hydrocarbons homologous with benzene are oxidised, each side-chain, no matter what its length or nature, yields only a single carboxyl group attached directly to the benzene nucleus. When several lateral chains are present, dilute nitric acid oxides them gradually, whilst with chromic acid they are all oxidised together: $C_6H_5 \cdot CH_3$ gives $C_6H_5 \cdot CO_2H$; $C_6H_5 \cdot C_2H_5$ gives $C_6H_5 \cdot CO_2H$; $C_6H_5 \cdot CH : CH \cdot CO_2H$ gives $C_6H_5 \cdot CO_2H$; $C_6H_4(CH_3)_2$ gives $C_6H_4(CO_2H)_2$. Of the disubstituted derivatives, the *ortho*-compounds are oxidised very easily and do not give carboxyls unless the oxidation is carried out with great care, *e.g.*, with dilute nitric acid or permanganate; *para*-derivatives are readily oxidised by chromic acid and the *meta*- less readily. Compounds containing a negative group, even OH, in the *ortho*-position are not oxidised even by chromic acid.

(*b*) By oxidising primary alcohols and aldehydes in the usual way.

(*c*) By hydrolysing nitriles: $C_6H_5 \cdot CN + 2H_2O = NH_3 + C_6H_5 \cdot COOH$. The *nitriles* are formed by distilling, *e.g.*, potassium phenylsulphonate, with potassium cyanide or ferrocyanide: $C_6H_5 \cdot SO_3K + KCN = K_2SO_3 + C_6H_5 \cdot CN$ (benzonitrile) or from the chlorides of compounds with side-chains: $C_6H_5 \cdot CH_2Cl + KCN = KCl + C_6H_5 \cdot CH_2 \cdot CN$ (benzyl cyanide). Nitriles can also be obtained from primary amines by diazotising and subjecting the diazo-compounds to Sandmeyer's reaction (*see* p. 670); also from the aldehydes by way of the oximes (*see* p. 246).

(*d*) By the action of CO_2 on monobromobenzene in presence of sodium (Kekulé), or by treating benzene or its homologues with phosgene ($COCl_2$) in presence of $AlCl_3$ (Friedel and Crafts):

$$C_6H_5Br + CO_2 + 2Na = C_6H_5 \cdot COONa + NaBr;$$
$$C_6H_6 + COCl_2 = HCl + C_6H_5 \cdot CO \cdot Cl \text{ (which, with } H_2O\text{, gives the acid).}$$

(*e*) **Phenolic acids** are obtained by the action of CO_2 or CCl_4 and alkali on *sodium phenoxides*:

$$C_6H_5 \cdot ONa + CO_2 = C_6H_4{<}^{OH}_{COONa}$$

$$C_6H_5 \cdot ONa + CCl_4 = C_6H_4{<}^{OH}_{CCl_3} + NaCl, \text{ and}$$

$$C_6H_4{<}^{OH}_{CCl_3} + 4NaOH = 3NaCl + 2H_2O + C_6H_4{<}^{OH}_{COONa} \text{ (para).}$$

If chloroform is used in place of carbon tetrachloride, ortho- and para-hydroxyaldehydes are obtained.

(*f*) The syntheses with ethyl acetoacetate or ethyl malonate are analogous to those of the fatty series (*see* pp. 368 and 397) and are carried out with phenols, derivatives with halogens in the side-chain, etc.; complex ketonic acids are obtained which undergo both the acid and the ketonic decomposition.

Aromatic acids with unsaturated side-chains are obtained by the methods used for aliphatic unsaturated acids, or by Perkin's reaction (*see* p. 352) between fatty acids and aromatic aldehydes in presence of acetic anhydride, which removes the water formed:

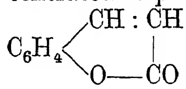
$$C_6H_5 \cdot CHO + \underset{\text{Sodium acetate}}{CH_3 \cdot CO_2Na} = C_6H_5 \cdot CH : CH \cdot COONa + H_2O.$$

With substituted benzaldehydes a varied series of unsaturated aromatic acids can be obtained.

Also benzal chloride and sodium acetate give unsaturated acids :

$$C_6H_5 \cdot CHCl_2 + CH_3 \cdot COOH = 2HCl + \underset{\text{Cinnamic acid}}{C_6H_5 \cdot CH : CH \cdot COOH}.$$

Ethyl acetoacetate and also malic acid act on phenols in presence of concentrated sulphuric acid, giving anhydrides of unsaturated phenolic acids, *e.g.*,


(*coumarin*).

(*a*) MONOBASIC AROMATIC ACIDS

The isomerism among these compounds is similar to that of the halogen derivatives of aromatic hydrocarbons.

BENZOIC ACID, $C_6H_5 \cdot COOH$, is found naturally in various resins (*e.g.*, gum benzoin) and in balsam of Tolu, from which it is obtained by sublimation or by heating with milk of lime. It is formed in the urine of herbivorous animals as **Hippuric acid**, which gives glycocoll and benzoic acid on putrefaction or when heated with acid or alkali. It forms white leaflets, sp. gr. 1·292, melting at 121·4°, and boils at 249·2° ; it sublimes at 100° to 120° and distils in steam. It has an irritating odour and is soluble in boiling water ; its alkali salts crystallise well ($C_6H_5 \cdot CO_2K + \frac{1}{2}H_2O$) and dissolve in water.

It is prepared industrially by converting toluene (from light tar oils), by means of chlorine, in presence of a little powdered iron, into benzenyl trichloride, $C_6H_5 \cdot CCl_3$, and heating this with milk of lime under pressure : $2C_6H_5 \cdot CCl_3 + 4Ca(OH)_2 = 3CaCl_2 + (C_6H_5 \cdot COO)_2Ca + 4H_2O$ (with traces of chlorobenzoic acid). Instead of being treated with lime, the benzenyl trichloride may be oxidised directly with dilute nitric acid, in vessels fitted with stirrers, as long as hydrogen chloride is evolved, the benzoic acid being then distilled, allowed to crystallise, centrifuged, and purified by sublimation. Jessnitzer (Ger. Pat. 236,489 of 1910) proposes to oxidise with calcium hypochlorite instead of with nitric acid.

Benzonitrile, $C_6H_5 \cdot CN$, found in the middle tar oils, gives pure benzoic acid when hydrolysed (Ger. Pat. 109,122).

According to Ger. Pat. 136,410, benzoic and phthalic acids are readily obtainable by heating naphthol or other naphthalene derivative with fused or dissolved alkali in presence of metallic oxides (MnO_2, CuO, Fe_2O_3) ; the benzoic acid is separated from the mixture by distillation.

USES. Benzoic acid is used in medicine, in making certain aniline blues of the anthraquinone dye group, in the seasoning of tobacco, in printing textiles, and for preserving foodstuffs,[1] although it has not been shown to be harmless when used in this way ; experiments made in the United States in 1910 showed that doses of 1 grm. per day of benzoic acid or sodium benzoate have no injurious effect. It cost about 3*s.* to 4*s.* per kilo before the war, and as much as 32*s.* during the war.

BENZOIC ANHYDRIDE, $(C_6H_5 \cdot CO)_2O$, is obtained by heating an alkali benzoate with benzoyl chloride :

$$C_6H_5 \cdot CO_2Na + C_6H_5 \cdot CO \cdot Cl = NaCl + (C_6H_5 \cdot CO)_2O,$$

[1] Of the various methods for detecting benzoic acid in foods, the following may be mentioned. According to Jonescu (1909) the presence of benzoic acid in *milk* may be shown by converting it into *salicylic acid* by means of 3 per cent. hydrogen peroxide diluted ten times, and then testing for salicylic acid with ferric chloride solution (sp. gr. 1·28) diluted ten times (as in the examination of beer). In the case of *butter* or *margarine* this is acidified with sulphuric acid and distilled with steam, the distillate being tested as above (*see also* Salicylic Acid).

MONOBASIC AROMATIC ACIDS

Formula.	Name.	Position of the groups.	Melting-point.
$C_6H_5 \cdot CO_2H$	Benzoic (benzenecarboxylic)	—	121°
$CH_3 \cdot C_6H_4 \cdot CO_2H$	*o*-Toluic (*o*-methylbenzenecarboxylic)	1 : 2	105°
,,	*m*- ,, (*m*- ,,)	1 : 3	111°
,,	*p*- ,, (*p*- ,,)	1 : 4	179°
$C_6H_5 \cdot CH_2 \cdot CO_2H$	Phenylacetic	—	76°
$C_6H_3(CH_3)_2 \cdot CO_2H$	Hemellitic	1 : 2-3	144°
,,	*o*-Xylic (1-CH_3 ; 2-CH_3 : 4-CO_2H)	1 : 2-4	166°
,,	*m*- ,, (*vic.*)	1 : 3-2	98°
,,	*m*- ,, (*as.*)	1 : 3-4	126°
,,	Mesitylenic	1 : 3-5	166°
,,	*p*-Xylic	1 : 4-2	132°
$C_6H_5 \cdot CH_2 \cdot CH_2 \cdot CO_2H$	Hydrocinnamic	–	49°
$C_6H_5 \cdot CH(CH_3) \cdot CO_2H$	Hydratropic (methylphenylacetic)	—	below — 20° (b.-pt. 267°)
$C_2H_5 \cdot C_6H_4 \cdot CO_2H$	*o*-Ethylbenzoic	1 : 2	68°
,,	*p*- ,,	1 : 4	112°
$C_6H_2(CH_3)_3 \cdot CO_2H$	Prehnitylic (trimethylbenzenecarboxylic)	1 : 2 : 3-4	168°
,,	*α*-Isodurylic ,,	1 : 2 : 3-5	215°
,,	Durylic ,,	1 : 2 : 4-5	149°
,,	γ-Isodurylic ,,	1 · 2 : 4-6	127°
,,	Mesitylenecarboxylic ,,	1 : 3 : 5-2	152°
$C_3H_7 \cdot C_6H_4 \cdot CO_2H$	Cuminic (*p*-isopropylbenzoic)	1 : 4	117°
$C_6H(CH_3)_4 \cdot CO_2H$	Prehnitenecarboxylic (tetramethylbenzoic)	1: 2 : 3 : 4-5	165°
,,	Isodurenecarboxylic ,,	1 : 2 : 3 : 5-4	161°
,,	Durenecarboxylic ,,	1 : 2 : 4 : 5-3	179°
$C_6(CH_3)_5 \cdot CO_2H$	Pentamethylbenzoic	1 : 2 : 3 : 4 : 5 : 6	210·5°
$C_6H_5 \cdot CH : CH \cdot CO_2H$	Cinnamic	—	133° (b.-pt. 300°)
$C_6H_5 \cdot C(: CH_2) \cdot CO_2H$	Atropic	—	107° (b.-pt. 267°)
$C_6H_5 \cdot C : C \cdot CO_2H$	Phenylpropioli	—	137°
$OH \cdot C_6H_4 \cdot CH : CH \cdot CO_2H$	*o*-Coumaric	1 : 2	208°
,,	*p*- ,,	1 : 4	206°
$OH \cdot C_6H_4 \cdot CO_2H$	*o*-Hydroxybenzoic (salicylic)	1 : 2	159°
,,	*m*- ,, ,,	1 : 3	200°
,,	*p*- ,, ,,	1 : 4	210°
$CH_3O \cdot C\ H_4 \cdot CO_2H$	Anisic	1 : 4	184°
$CH_3 \cdot C_6H_3(OH) \cdot CO_2H$	*o*-Hydroxytoluic	1 : 2-3	164°
,,	*m*- ,,	1 : 3-4	177°
,,	*p*- ,,	1 : 4-3	151°
,,	*β*-*m*- ,,	1 : 3-2	168°
$OH \cdot C_6H_4 \cdot CH_2 \cdot CH_2 \cdot CO_2H$	Hydro-*p*-coumaric	1 : 4	118°
$C_6H_5 \cdot CH(OH) \cdot CO_2H$	Mandelic	—	118°
$C_6H_5 \cdot CH(CH_2 \cdot OH) \cdot CO_2H$	Tropic	—	117°
$C_6H_5 \cdot CO \cdot CO_2H$	Benzoylformic	—	65°
$C_6H_5 \cdot CO \cdot CH_2 \cdot CO_2H$	Benzoylacetic	—	103°
$C_6H_3(OH)_2 \cdot CO_2H$	Protocatechuic	1 : 3-4	199°
$C_6H_3(CH_3)(OH)_2 \cdot CO_2H$	Orsellinic (1-methyl-3 : 5 dihydroxybenzene -2-carboxylic)	1 : 3 : 5-2	176°
$C_6H_2(OH)_3 \cdot CO_2H$	Gallic (3 : 4 : 5-trihydroxybenzenecarboxylic)	3 : 4 : 5-1	221°

or, according to Ger. Pat. 146,690, by heating nearly 2 parts of sodium chlorosulphonate, $Cl \cdot SO_3Na$, with 3 parts of sodium benzoate; by changing these proportions, benzoyl chloride (*see below*) may be obtained.

In the cold it is not decomposed by water, but on boiling it gives benzoic acid.

BENZOYL CHLORIDE, $C_6H_5 \cdot CO \cdot Cl$, is formed by the action of PCl_5 or $POCl_3$ on benzoic acid, and is obtained industrially either by the action of chlorine on benzaldehyde or from sodium chlorosulphonate (*see above*, Benzoic anhydride). It is a colourless liquid which boils at 194°, and has a very pungent odour. Water decomposes it very slowly in the cold (distinction from acetyl chloride), giving hydrochloric and benzoic acids. It reacts readily with many compounds in alkaline solution, introducing into them the benzoyl group (Schotten and Baumann's method). For instance, a mixture of benzoyl chloride with a little potassium hydroxide acts in the cold on aniline, forming **Benzanilide**, $C_6H_5 \cdot NH \cdot CO \cdot C_6H_5$ (white compound, melting at 158°, and boiling unaltered). With hydroxylamine it gives **Benzhydroxamic acid**, $C_6H_5 \cdot CO \cdot NH \cdot OH$, which gives a violet coloration with ferric chloride.

Benzoyl chloride is used in the preparation of benzaldehyde and of various dyes.

ETHYL BENZOATE, $C_6H_5 \cdot CO_2C_2H_5$, has an odour of mint, and is obtained by heating benzoic acid with alcohol in presence of sulphuric acid.

BENZAMIDE, $C_6H_5 \cdot CO \cdot NH_2$, is obtained by the action of ammonia (or ammonium carbonate) on benzoyl chloride, or by the interaction of sulphuric acid and benzonitrile. It forms nacreous crystals melting at 128°, and is soluble in boiling water. It forms metallic derivatives more easily than acetamide.

Dibenzamide, $(C_6H_5 \cdot CO)_2\,NH$, melts at 148°.

BENZHYDRAZIDE, $C_6H_5 \cdot CO \cdot NH \cdot NH_2$, is obtained from hydrazine hydrate and benzoic ester ; with nitrous acid, it gives

BENZAZIDE (**Benzoylazoimide**), $C_6H_5 \cdot CO \cdot N\langle {N \atop N} \|$, which is readily hydrolysed, giving hydrazoic and benzoic acids.

HIPPURIC ACID, $C_6H_5 \cdot CO \cdot NH \cdot CH_2 \cdot CO_2H$, is obtained by heating benzoic anhydride with glycocoll. It occurs in the urine after ingestion of benzoic acid or toluene, and is found in considerable quantities in the urine of horses and other herbivorous animals. It forms rhombic crystals melting at 187°, and is soluble in hot water.

CHLOROBENZOIC ACIDS, $C_6H_4Cl \cdot CO_2H$. The halogen enters preferably the meta-position,[1] and nitric acid (in presence of concentrated sulphuric acid) gives mainly *m*-**Nitrobenzoic acid**, $NO_2 \cdot C_6H_4 \cdot CO_2H$,[2] which, on reduction, yields **Azobenzoic acids** and **Aminobenzoic acids**, $NH_2 \cdot C_6H_4 \cdot CO_2H$. The latter, like glycine, exhibit the functions of both acids and bases ; with nitrous acid, they form **Diazobenzoic acids**, $C_6H_4 < {N:N \atop CO_2} >$.

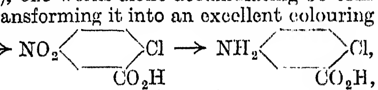
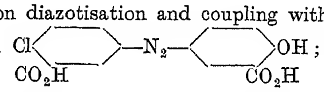
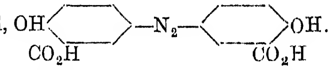
Polysubstituted benzoic acids, having the substituents (Cl, Br, NO_2, CH_3, CO_2H, etc.) in the ortho-position with respect to the carboxyl, give no esters when treated with alcohol and hydrochloric acid, such acids being hence separable in this way.

ANTHRANILIC ACID (*o*-**Aminobenzoic acid**), $NH_2 \cdot C_6H_4 \cdot CO_2H$, serves for making synthetic indigo and many azo colouring matters, drugs and perfumes, especially thiosalicylic acid and methyl anthranilate.[3] It has m.-pt. 145° and sublimes readily ; it has a very sweet taste and, when distilled, decomposes into CO_2 and aniline.

Its formation by the intramolecular transposition of *o*-nitrophenol is of interest, although it is not of practical utility. It is best obtained by treating phthalimide with the theoretical proportions of sodium hypochlorite and caustic soda : $C_6H_4 \langle {CO \atop CO} \rangle NH + NaOCl + 3NaOH = H_2O + NaCl + Na_2CO_3 + NH_2 \cdot C_6H_4 \cdot CO_2Na$. It forms an internal anhydride, termed *anthranil*, $C_6H_4 \langle {CO \atop NH} | $.

Of the dibasic **Sulphobenzoic acids**, $C_6H_4(SO_3H)(CO_2H)$, the ortho-isomeride is of interest, since its imino-derivative forms **SACCHARIN** (*o*-**Benzoicsulphimide**), $C_6H_4 < {SO_2 \atop CO} > NH$, which is a white crystalline substance exhibiting marked phosphorescence when its crystals are fractured. It melts at 224° with partial decomposition, and sublimes unaltered in a vacuum. It dissolves slightly in cold water and to a greater extent in cold alcohol ; its heat of combustion is 4751·3 cals.

Saccharin is about 550 times as sweet as sugar but is rapidly eliminated unchanged from

[1] *o-Chlorobenzoic acid*, m.-pt. 140°, b.-pt. 287°, is formed in appreciable amount as a bye-product in the manufacture of benzaldehyde (*see* p. 674), one works alone accumulating 30 tons in a few years. A few years ago Mettler succeeded in transforming it into an excellent colouring matter, *eriochromoflavine A*, $C_6H_4Cl \cdot CO_2H + HNO_3 \longrightarrow$  which on diazotisation and coupling with salicylic acid gives an azo dyestuff of little value, namely,  ; when the latter is heated at 135° with potash and a little copper oxide, it gives *eriochromoflavin* or *azosalicylic* acid, .

[2] *m-Nitrobenzoic acid*, m.-pt. 144°, sp. gr. 1·494, gives, on reduction with iron and acetic acid, *m-aminobenzoic acid*, m.-pt. 174°, sp. gr. 1·51, which is used in making azo dyestuffs.

s-Trinitrobenzoic acid melts at 210° with evolution of CO_2 and formation of trinitrobenzene, and is obtained by oxidising trinitrotoluene with either nitric and sulphuric acids, or nitric acid and potassium chlorate, or chromic and sulphuric acids. When boiled with water it is converted completely into trinitrobenzene.

[3] *Methyl anthranilate* has m.-pt. 24·5°, b.-pt. 135·5°, occurs in neroli and jessamine oils, and has a pronounced odour of orange blossoms and mandarins.

Methyl methylanthranilate, $CO_2CH_3 \cdot C_6H_4 \cdot NH \cdot CH_3$, m.-pt. 19°, b.-pt. 130°, occurs in mandarin oil and has a feebler odour than the preceding ester.

the animal system. It behaves as an energetic acid, being able to decompose carbonates and acetates, forming salts, all of which are very sweet; the sodium salt, $C_6H_4<^{SO_2}_{CO}>NNa + 2H_2O$, is used as a sweetening agent owing to its solubility in water. It was discovered accidentally by Fahlberg and Remsen in 1879, being obtained by the oxidation of *o*-toluene-sulphamide, $NH_2 \cdot SO_2 \cdot C_6H_4Me$. Its manufacture was gradually improved by Hempel and especially by Heyden, and the price fell to 12*s*. per kilo before the European War.[1]

Paul (1920) found that the sweetening power of saccharin may be increased by admixture with certain other substances, such as *dulcin*, $NH_2 \cdot CO \cdot NH \cdot C_6H_4 \cdot OC_2H_5$, m.-pt. 173°, which is obtained by heating urea with *p*-phenetidine and is itself 200 times as sweet as sugar.

In large doses saccharin has an antifermentative action, but it is harmless in the small amounts usually introduced into foods. In some countries its use has been prohibited for fiscal or supposed hygienic reasons. An International Convention at Brussels in 1909 passed a resolution that all countries should prohibit the use of saccharin in foods and beverages and place severe restrictions on its sale.

TOLUIC ACIDS, $CH_3 \cdot C_6H_4 \cdot COOH$. The three isomerides are obtained by oxidising the corresponding xylenes with dilute nitric acid (*see* Table, p. 681). *p*-Toluic acid is formed also by the oxidation of turpentine.

Phenylacetic acid (*a-Toluic acid*), $C_6H_5 \cdot CH_2 \cdot CO_2H$, is isomeric with the toluic acids, but it gives benzoic acid on oxidation, whereas the toluic acids give *phthalic acids*.

XYLIC ACIDS, $C_6H_3(CH_3)_2 \cdot CO_2H$; various isomerides are known (*see* Table, p. 681).

CUMINIC ACID (*p*-**Isopropylbenzoic acid**), **$C_3H_7 \cdot C_6H_4 \cdot CO_2H$**, is formed in animal organisms by the oxidation of cymene, and is obtained by oxidation of Roman chamomile oil with permanganate. It melts at 117° and yields cumene when distilled with lime.

CINNAMIC ACID, $C_6H_5 \cdot CH : CH \cdot CO_2H$, is found in storax and in certain balsams (Tolu, Peru, etc.), and remains as sodium salt when these are distilled with caustic soda. It is prepared according to Perkin's synthesis (p. 352) by heating benzaldehyde with sodium acetate in presence of a dehydrating agent (acetic anhydride); or by heating benzylidene chloride (benzal chloride) with sodium acetate in an autoclave at 200°; or by the malonic synthesis from benzaldehyde and ammonia:

$$C_6H_5 \cdot CHO + CH_2(COOH)_2 = H_2O + CO_2 + C_6H_5 \cdot CH : CH \cdot COOH.$$

Cinnamic acid melts at 133° and boils at about 300°. It readily forms additive products owing to the double linking in the side-chain, and on this account also reduces permanganate in presence of sodium carbonate (Baeyer's reaction, p. 107).

According to theory, the presence of the double linking should result in the existence of two stereoisomerides:

$$\begin{array}{c} C_6H_5 \cdot C \cdot H \\ \| \\ H \cdot C \cdot CO_2H \end{array} \quad \text{and} \quad \begin{array}{c} C_6H_5 \cdot C \cdot H \\ \| \\ CO_2H \cdot C \cdot H, \end{array}$$

but, in addition to these, two others, **Allocinnamic** (m.-pt. 68°) and **Isocinnamic acids** (m.-pt. 58° to 62°), are known and have been studied by Liebermann,

[1] The method now used for making saccharin is as follows: pure toluene is treated in the cold with chlorosulphonic acid, a mixture of toluene ortho- (35 per cent.) and para- (65 per cent.) sulphochlorides being obtained. The mixture of sulphochlorides is cooled to a low temperature and centrifuged to separate the crystalline para-compound (m.-pt. 69°) from the liquid ortho-compound, which distils unaltered in a vacuum at 126° and has the sp. gr. 1·3443 at 17°. By treatment with ammonia the latter is converted into *o*-toluenesulphamide, which is oxidised by permanganate to the potassium salt of *o*-benzenesulphaminic acid; the action of an acid on this then results in the formation of saccharin. The oxidation of the sulphamide may also be effected by means of dichromate and sulphuric acid.

Michael, and Erlenmeyer, jun. Biilmann (1909) shows allocinnamic and the two isocinnamic acids to be merely trimorphous modifications of one and the same chemical individual—the cis-acid—so that they are identical in the fused or dissolved state. Previous failures to separate the three crystalline forms were due to the difficulty of excluding minute crystals of the common form from the solutions ; this was finally overcome by the use of cotton-wool plugs.

Cinnamic acid cost before 1913 16*s*. per kilo, and it is used in medicine and in the synthesis of various perfumes.

PHENYLPROPIOLIC ACID, $C_6H_5 \cdot C \vdots C \cdot CO_2H$, is obtained by heating the dibromide of ethyl cinnamate with alcoholic potash :

$$C_6H_5 \cdot CHBr \cdot CHBr \cdot CO_2C_2H_5 + H_2O = 2HBr + C_6H_5 \cdot C \vdots C \cdot CO_2H + C_2H_5 \cdot OH.$$

It forms shining needles which melt at 137° and readily sublimes. Its sodium salt is used in 1 to 3 per cent. solution as an inhalation in cases of tuberculosis, and cost £4 per kilo prior to the European War. *o*-Nitrophenylpropiolic acid, obtained in a similar manner from ethylo-nitrocinnamate, is used in the synthesis of indigo.

(*b*) DIBASIC AND POLYBASIC AROMATIC ACIDS

The basicity of these acids is given by the number of carboxyl groups, and the phenomena of isomerism are similar to those of the dihalogenated derivatives. The carboxyl groups may be united directly to the benzene nucleus or to side-chains, and by means of them esters, amides, acid chlorides, etc., can be formed.

PHTHALIC ACID (Phenylene-*o*-dicarboxylic acid), $C_6H_4 < {COOH(1) \atop COOH(2)}$, is obtained by oxidising compounds with two lateral chains, but not by chromic acid, which would partially destroy the benzene nucleus.

At one time it was prepared industrially by chlorinating naphthalene and then oxidising (Laurent), but for some years it has been obtained more conveniently by oxidising naphthalene with fuming sulphuric acid in presence of mercury salts or, better, rare earth salts (thorium, etc.), which act as catalysts.

This catalytic process, which is due to Sapper, allows of the recovery of the whole of the mercury, while the sulphur dioxide evolved is converted again into sulphur trioxide, so that the oxidation of the naphthalene may be regarded as taking place at the expense of the oxygen of the air. This economical process has rendered possible the industrial preparation of artificial indigo.

The process of fusing naphthols with alkali in presence of metallic oxides also seems to give good results and yields benzoic acid at the same time (*see above*). According to Ger. Pat. 152,063, the electrolysis of naphthalene in presence of an acid solution of a cerium compound yields naphthaquinone and phthalic acid.

When phthalic acid is substituted in the ortho-position, that is, adjacent to one of the carboxyl groups, only one of the latter can be esterified.

It is a white, crystalline substance soluble in hot water, alcohol, and ether. It melts at 213° and is then transformed into Phthalic anhydride, $C_6H_4 < {CO \atop CO} > O$, which melts at 128° and boils at 277°, but sublimes considerably below this temperature ; the anhydride has a characteristic odour and gives phthalic acid when boiled with water.

With PCl_5, phthalic acid gives Phthalyl chloride, $C_6H_4 < {CCl_2 \atop CO} > O$, which gives Phthalide, $C_6H_4 < {CH_2 \atop CO} > O$, on reduction, and Phthalophenone, $C_6H_4 < {C(C_6H_5)_2 \atop CO} > O$, with benzene ($+ AlCl_3$).

When heated with phenols and sulphuric acid, phthalic anhydride forms *phthaleins, e.g.*,

$$C_6H_4<^{CO}_{CO}>O + 2C_6H_5 \cdot OH = H_2O + C_6H_4<^{C(C_6H_4 \cdot OH)_2}_{CO}>O \text{ (phenolphthalein)}.$$

Phenolphthalein is a yellow powder and, being a phenol, dissolves in alkali, the solution having a violet-red colour (it forms an excellent indicator, *see* Vol. I., p. 100). When heated with resorcinol in presence of zinc chloride at 210°, phthalic anhydride yields **Fluorescein** (*resorcinolphthalein*),

$$CO<^{C_6H_4}_{-O-}>C<^{C_6H_3(OH)}_{C_6H_3(OH)}>O,$$

which, even in very dilute alkaline solution, shows an intense greenish yellow fluorescence, while by transmitted light the solution appears reddish (*see* Triphenylmethane Dyes).[1]

Tetrabromofluorescein, or *eosin*, gives alkaline solutions showing a marked reddish green-yellow fluorescence, and is used for dyeing silk red, producing a beautiful fluorescent effect; the colour is, however, not very stable, especially towards light.

With dry ammonia in the hot, phthalic anhydride gives **Phthalimide**, $C_6H_4<^{CO}_{CO}>NH$, which is of importance since the iminic hydrogen can be replaced by metals and the latter, under the action of alkyl halides, by alkyl groups. The compounds thus obtained, when heated with acid or alkali, yield phthalic acid and a *primary amine* free from secondary or tertiary amine (important general synthesis of primary amines, discovered by Gabriel):

$$C_6H_4<^{CO}_{CO}>NK + C_2H_5Br = KBr + C_6H_4<^{CO}_{CO}>NC_2H_5, \text{ and}$$

$$C_6H_4<^{CO}_{CO}>NC_2H_5 + 2H_2O = C_6H_4<^{CO_2H}_{CO_2H} + C_2H_5 \cdot NH_2.$$

Phthalic acid is used in the synthesis of indigo and of dyes of the pyronine group, and is usually placed on the market as the anhydride (although called acid) at a pre-war price of £60 per ton (65 per cent. strength); chemically pure, it cost 4*s*. per kilo.

ISOPHTHALIC ACID, $C_6H_4(CO_2H)_2(1:3)$, is obtained by oxidation of colophony with nitric acid, or, in general, by the oxidation of meta-derivatives of benzene. The barium salt is soluble in water.

TEREPHTHALIC ACID, $C_6H_4(CO_2H)_2(1:4)$, is formed by oxidising oil of turpentine or chamomile oil, or by oxidising *p*-toluic acid with permanganate. It is almost insoluble in water and alcohol and sublimes unchanged. It gives a sparingly soluble barium salt, but does not form an anhydride.

POLYBASIC ACIDS. The tri-, tetra-, penta-, and hexa-carboxylic acids are known, but are of little practical importance.

The **Benzenetricarboxylic Acids** are: **Trimesic acid** (1 : 3 : 5), derived from mesitylene; **Trimellitic acid** (1 : 2 : 4), obtained from colophony; **Hemimellitic acid** (1 : 2 : 3).

The **Benzenetetracarboxylic Acids** are: **Pyromellitic acid** (1 : 2 : 4 : 5), melting at 264°; **Prehnitic acid** (1 : 2 : 3 : 4), melting at 237° and forming an anhydride; **Mellophanic acid** (1 : 3 : 4 : 5), which melts, and is converted into anhydride, at 280°.

MELLITIC ACID (**Benzenehexacarboxylic acid**), $C_6(COOH)_6$, is obtained from mellite, which is a kind of mineral found in deposits of lignite, and consists of yellow, quadratic octahedra of aluminium mellitate, $C_6(COO)_6Al_2 + 18H_2O$.

Mellitic acid may also be obtained by oxidising wood charcoal with alkaline permanganate. It forms needles insoluble in water and alcohol and, when heated, loses $2H_2O$ and $2CO_2$, forming **Pyromellitic anhydride**, $O<^{\overset{1}{CO}}_{\underset{2}{CO}}>C_6H_2<^{\overset{4}{CO}}_{\underset{5}{CO}}>O$, which gives **Pyromellitic acid**, $C_6H_2(CO_2H)_4$, with water.

[1] This property is sometimes utilised to ascertain if underground watercourses communicate with one another and to detect infiltrations into wells.

Mellitic acid cannot form substitution products, since all the benzene hydrogens are already substituted, but on reduction with sodium amalgam it readily yields **Hydromellitic acid**, $C_6H_6(COOH)_6$, which gives benzene when distilled with lime.

(c) HYDROXY-ACIDS OR PHENOLIC ACIDS

These are formed by the methods given on p. 679 or by oxidising homologues of phenol or fusing them with alkali. The basicity is given by the number of carboxyl and phenolic groups, both of these leading to salt-formation, but the basicity towards sodium carbonate is determined by the carboxyl groups alone. When both the carboxyl and hydroxyl groups are etherified, only the former can be subsequently hydrolysed.

SALICYLIC ACID (*o*-**Hydroxybenzoic acid**), $OH \cdot C_6H_4 \cdot COOH$, is the most important of the hydroxy-acids, and was discovered by Piria in 1839 and prepared in 1885 by treating salicylaldehyde with alkali.

Kolbe established its constitution in 1853 from its ready decomposition into CO_2 and phenol, and in 1860 synthesised it from these products in presence of metallic sodium.

It is derived from *salicin* (glucoside of willow bark), which, when hydrolysed, first gives glucose and **Saligenin** :

$$\underset{\text{Salicin}}{C_6H_4{<}{\begin{smallmatrix}O \cdot C_6H_{11}O_5\\ CH_2 \cdot OH\end{smallmatrix}}} + H_2O = \underset{\text{Saligenin}}{C_6H_4{<}{\begin{smallmatrix}OH\\ CH_2 \cdot OH\end{smallmatrix}}} + \underset{\text{Glucose}}{C_6H_{12}O_6},$$

the saligenin giving salicylic acid on oxidation. The acid is found as methyl ester in the essence of *Gaultheria procumbens*.

It is prepared industrially by heating sodium phenoxide with carbon dioxide in an autoclave at 140°, according to Kolbe's process ; from the resulting sodium salicylate the acid is liberated by treatment with a mineral acid. In Marasse's method a mixture of phenol and potassium carbonate is heated in presence of CO_2 at 140° to 160°, but the yields are very low. Only later, when the conditions of the reaction were studied, were the yields and quality of the product improved.

By the action of CO_2 in the hot, sodium phenoxide is converted, to the extent of one-half, into the salicylate, $NaO \cdot C_6H_4 \cdot CO_2Na$, whereas potassium phenoxide yields the para-compound, p-$KO \cdot C_6H_4 \cdot CO_2K$. In the first case the reaction begins at 100° and the yield increases up to 180°, no further increase occurring even up to 300°; with the potassium compound, the ortho-dipotassium salicylate is formed at 100° to 150°, the para-isomeride being formed as the temperature is raised and constituting the sole product at 220°. At the latter temperature monopotassium salicylate is transformed into the para-dipotassium compound, $2OH \cdot C_6H_4 \cdot CO_2K = CO_2 + C_6H_5 \cdot OH + OK \cdot C_6H_4 \cdot CO_2K$, whereas under no conditions does monosodium salicylate give the para-isomeride. The monosodium para-salt may be obtained otherwise, and at 290° gives phenol, CO_2 and disodium salicylate.

According to Schmitt, phenol may be converted wholly into salicylic acid by the action of CO_2 at the ordinary temperature on sodium phenoxide, the *sodium phenyl carbonate*, $C_6H_5 \cdot CO_3Na$, thus formed yielding sodium salicylate when heated out of contact with the air. S. Tymstra, jun., showed, however (1905—1912), that the final product formed in this process is **o-Oxysodiobenzoic acid**, $ONa \cdot C_6H_4 \cdot CO_2H$, which arises by simple addition of CO_2.

On the basis of these results the more economical and rational method of manufacture now in use has been developed, the various phases of the reaction being carried out in an autoclave provided with a stirrer and with either a double jacket or coils through which steam or water may be passed.

Salicylic acid forms white crystals melting at 156·8°, subliming at 200°, and distilling in superheated steam at 170°. It is readily soluble in alcohol or in ether, and 1 part dissolves in 444 parts of water at 15° and in 13 parts of hot

water. It has a sweetish astringent taste. When heated with $POCl_3$ it gives the **Internal anhydride**, $C_6H_4\left<\begin{matrix}O\\|\\CO\end{matrix}\right.$, which forms a white powder softening at 110° and melting at 261°.

With bromine water it gives a precipitate, $C_6H_2Br_3 \cdot OBr$, and with ferric chloride it gives a violet coloration even in alcoholic solution (phenol is coloured only in aqueous solution). With lime-water in the hot it forms a basic salt, $C_6H_4<\begin{matrix}-O-\\COO\end{matrix}>Ca$, and can thus be separated from its isomerides, which do not give this reaction.

It is used as an antiseptic for preserving foodstuffs,[1] and in the manufacture of dyes and perfumes. Its sodium salt is largely used as a medicine.

When heated to 200° it loses CO_2, giving **Phenyl salicylate** (*salol*):

$$2OH \cdot C_6H_4 \cdot CO_2H = CO_2 + H_2O + OH \cdot C_6H_4 \cdot CO_2C_6H_5,$$

which is used as an antiseptic for the intestines; it melts at 42° and boils at 172° in a vacuum. Industrially it is obtained by heating a mixture of sodium salicylate, sodium phenoxide and phosphorus oxychloride (or phosgene) at 125°, the product being washed with water, decolorised with animal charcoal and crystallised from alcohol.

ACETYLSALICYLIC ACID, $C_2H_3O \cdot O \cdot C_6H_4 \cdot CO_2H$, prepared by heating salicylic acid with acetic anhydride and sulphuric acid, is largely used under the name **ASPIRIN** as an antipyretic, antineuralgic and analgesic. It has an acid taste and forms lustrous, white crystals, melting at 135° and solidifying at 118°. Unlike salicylic acid and salol, it gives no coloration with ferric chloride, and it passes unchanged through the stomach but undergoes decomposition in the intestines.

m- and *p*-**HYDROXYBENZOIC ACIDS** give insoluble basic barium salts and yield no coloration with ferric chloride; the *m*-acid is more stable to heat than the *o*- or *p*-acid.

Anisic acid, $CH_3O \cdot C_6H_4 \cdot CO_2H$, resembles the monobasic acids more than the phenols and is obtained from *p*-hydroxybenzoic acid, methyl alcohol, potassium hydroxide, and methyl iodide, the dimethyl ether obtained being then partially hydrolysed.

Methyl salicylate, $OH \cdot C_6H_4 \cdot CO_2CH_3$, forms 90 per cent. of oil of Gaultheria, and is prepared artificially by the interaction of salicylic acid (2 parts) and methyl alcohol (2 parts) in presence of concentrated sulphuric acid (1 part). It boils at 224° and is used as a perfume.

p-**HYDROXYPHENYLACETIC ACID, $OH \cdot C_6H_4 \cdot CH_2 \cdot CO_2H$,** formed during the putrefaction of proteins and occurring in the urine, gives a dirty green coloration with ferric chloride.

Of the **Dihydroxybenzoic acids, PROTOCATECHUIC ACID** (**3 : 4-Dihydroxybenzoic acid**), $C_6H_3(OH)_2 \cdot CO_2H$, forms shining scales or crystals soluble in water; in solution it is coloured green by ferric chloride, the colour being changed to blue and then to red by a little soda. It can be obtained synthetically, together with the 2 : 3-dihydroxy-acid, by heating catechol with ammonium carbonate, and is prepared by fusing various resins with alkali. Like catechol, it exhibits reducing properties. Its monomethyl ether ($3\text{-}OCH_3$) is **VANILLIC ACID**, which is formed by the oxidation of vanillin (p. 677); its dimethyl ether [$(OCH_3)_2$] is **VERATRIC ACID**, found in the seeds of *Veratrum Sabadilla*, and its **Methylene ether**, $CO_2H \cdot C_6H_3<\begin{matrix}O\\O\end{matrix}>CH_2$, is **PIPERONYLIC ACID**, which is also obtained by oxidising piperinic acid.

[1] The examination of foods for the presence of salicylic acid is carried out in the same way as with beer (p. 212), but baked starchy substances (bread, etc.) contain *maltol*, which gives the same reaction as salicylic acid and is, like the latter, volatile. In this case Jorissen's method must be used in testing for salicylic acid: 10 c.c. of the liquid distilled with steam is treated with 5 drops of 10 per cent. potassium nitrite solution, 5 drops of 50 per cent. acetic acid, and 1 drop of 10 per cent. copper sulphate solution. The liquid is then boiled, and in presence of even less than 0·0001 grm. of salicylic acid a reddish coloration forms, which rapidly becomes blood-red (H. C. Sherman, 1910).

GALLIC ACID (3 : 4 : 5-Trihydroxybenzenecarboxylic acid), $C_6H_2(OH)_3 \cdot CO_2H$, occurs naturally as glucosides in various plants and in tea, gall-nuts, etc. It is formed by the action of mould on solutions of tannin or by boiling the latter with dilute acid or caustic soda.

It reduces gold and silver salts and becomes oxidised and turns brown in the air. With ferric chloride it gives a black coloration, and, on this account, it is used in making ink [1]; its reducing properties are utilised in photography.

When pure it forms colourless needles ($+ H_2O$) which at 120° lose the water of crystallisation and melt at 220° to 240°; when distilled it decomposes into carbon dioxide and pyrogallol. It is only slightly soluble in ether or cold water but dissolves readily in alcohol or hot water. It reduces Fehling's solution, gives a bluish-black coloration with ferric chloride, and in alkaline solution absorbs atmospheric oxygen and becomes brown.

It is used in making pyrogallol, dyes of the anthraquinone (*anthracene brown*, etc.) and gallocyanin and galloflavin groups, inks and drugs: *airol*, $C_6H_2(OH)_3 \cdot CO_2BiI \cdot OH$, used on wounds instead of iodoform, is odourless and non-irritant; *dermatol*, $C_6H_2(OH)_3 \cdot CO_2Bi(OH)_2$, serves as an antiseptic for wounds, intestinal and stomach maladies, and for perspiring feet.

Gallic acid is made by treating gall-nuts with water and yeast at 38° to 40°, the mass being afterwards extracted with a mixture of 4 parts of ether and 1 part of alcohol, and the alcohol and ether carefully distilled off through a rectifying column. The crude gallic acid separating from the resulting aqueous solution is purified by treatment with albumin, decolorised by means of hydrosulphite and animal charcoal, and crystallised. Gallic acid may be obtained also by treating tannin (or the mother liquors from its preparation) with dilute sulphuric acid or with a pure culture of *Aspergillus gallomyces*.

There are a number of *hydroxy-acids* with hydroxyl and carboxyl groups in the side-chains; mention may be made of:

(1) COUMARIC ACID (*o*-Hydroxycinnamic acid), $OH \cdot C_6H_4 \cdot CH : CH \cdot CO_2H$, which does not give an anhydride owing to its fumaroid structure (*see* Fumaric acid), while the maleic stereoisomeride, **Coumarinic acid**, is known only as salts, since in the free state it immediately forms **Coumarin**, $C_6H_4\left\langle\begin{array}{l}O\text{---}CO\\ \quad\;\;\,|\\ CH:CH\end{array}\right.$; the latter may also be obtained by heating salicylic acid with sodium acetate (Perkin synthesis: *see* Aldehydes).

(2) MANDELIC ACID, $C_6H_5 \cdot CH(OH) \cdot CO_2H$; of the various stereoisomerides, that occurring naturally is lævo-rotatory, whilst that obtained synthetically (from benzaldehyde and hydrocyanic acid, with subsequent

[1] INK is made by adding to aqueous gallic acid or tannin ferrous sulphate solution slightly acidified with acetic or hydrochloric acid in order to prevent oxidation and the formation of a black precipitate. To this brownish solution is added a solution of indigo-carmine or logwood to render the writing visible. When the ink is exposed on the paper to the air, it becomes black and insoluble, owing to the evaporation or neutralisation of the acid by the sizing of the paper (albumen, etc.), and the consequent ready oxidation by atmospheric oxygen, which changes the original blue colour to a deep black.

To make the ink adhere without spreading, a little gum is added, and to preserve it, a little phenol (1 litre of this normal ink may be obtained from 23·4 grms. of tannin, 7·7 grms. of gallic acid, 10 grms. of gum, 7·5 grms. of concentrated hydrochloric acid, 30 grms. of ferrous sulphate, 1 grm. of phenol, and the rest water; the liquid is left at rest for four days and then decanted from the deposit and coloured with indigo-carmine or logwood extract).

A *logwood ink* may be obtained as follows: 20 grms. of dry logwood extract or 30 grms. of the paste (hæmateïn) are dissolved in 800 c.c. of water, and to the hot solution are added 15 grms. of soda crystals (7 grms. of Solvay soda), and then, drop by drop, and with shaking, 100 c.c. of a solution containing 1 grm. of normal potassium chromate; this process gives a fine blue-black tint, and the ink, which does not attack steel pens and dries easily, can be preserved by a trace of phenol.

Coloured inks are aqueous, gummy solutions of aniline dyes. Copying inks are similar to ordinary writing inks, but are more concentrated, and contain also glycerine, sugar, dextrin, calcium chloride, etc., by which the writing is kept moist for some time.

hydrolysis) is the racemic form. In solutions of the latter, certain Schizomycetes destroy the *d*- and leave the *l*-isomeride, whilst *Penicillium glaucum* destroys the *l*- and leaves the *d*-compound. Also, if the cinchonine salt of the racemic form is prepared, the *d*-salt crystallises out first.

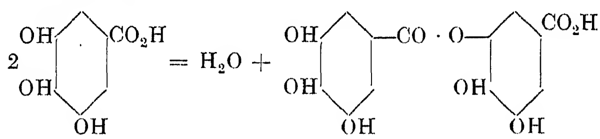
The **Dihydroxycinnamic acids** include: **CAFFEIC ACID** (*see* Chapter on Glucosides), **FERULIC ACID** and **UMBELLIC ACID** (*p*-hydroxy-*o*-coumaric acid, which is readily transformed into its anhydride, *umbelliferone*); a similar acid is **PIPERINIC ACID**,

$$CH_2{<}^{O}_{O}{>}C_6H_3 \cdot CH : CH \cdot CH : CH \cdot CO_2H,$$

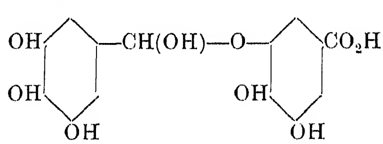
which is formed in the decomposition of piperine.

The derivatives of the **Trihydroxycinnamic acids** are dealt with in the Chapter on Glucosides (*æsculin* and *daphnin* from horse chestnuts and *Daphne mezereum*, etc., respectively). Mention may be made here of **ÆSCULETIN** (a **Dihydroxycoumarin**), $C_6H_2(OH)_2\begin{cases} O \cdot CO \\ \quad\ | \\ CH : CH \end{cases}$, and of the isomeric **DAPHNETIN**, which have also been obtained synthetically.

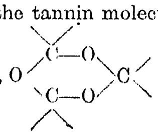
TANNIN (**Gallotannic or Tannic acid**), $C_{14}H_{10}O_9$, was studied originally by Berzelius, Pelouze, and Liebig. According to Hlasiwetz (1867) and to U. Schiff (1873), tannin is probably a partial and mixed anhydride of gallic acid, 2 mols. of which are condensed with loss of 1 mol. of water from a carboxyl and a hydroxyl group and formation of a **Digallic acid** (or ether of 3-*gallolylgallic acid*):



According to the investigations of Nierenstein (1908) on the acetyl-derivatives and hydrolysis, commercial tannin would seem to be a mixture of digallic acid and **Leucotannin** (or ether of 3-*hydroxygallolylgallic acid*):



There appear, however, to be various more or less highly polymerised tannins with widely varying molecular weights. Some uncertainty still prevails as to the true molecular magnitude of tannin. Paternò (1907, 1913) found that in aqueous solutions tannin acts as a colloid and by cryoscopic measurements on acetic acid solutions arrived at the formula, $C_{14}H_{10}O_9$ (mol. wt. 322), whilst Walden (1898), by the ebullioscopic method, obtained numbers between 760 (about C_{35} . . . .) and 1560 (about C_{70} . . . .), which are sharply distinguished from that of digallic acid (332).[1]

[1] P. Biginelli (1911), on the basis of the property shown by tannin of forming additive products with water, alcohol and ether [*e.g.*, $C_{41}H_{32}O_{25}$, $C_4H_{10}O$ (ether), which is stable even in a vacuum and is analogous to the oily compound, $C_{41}H_{32}O_{25}$, $6C_4H_{10}O$, $7H_2O$, previously obtained by Pelouze, and to others of Biginelli's compounds, namely, $C_{41}H_{32}O_{25}$, $6C_4H_{10}O$; $C_{41}H_{32}O_{25}$, $6C_2H_5 \cdot OH$; and $C_{41}H_{32}O_{25}$, $5H_2O$], and also on the loss of CO_2 and H_2O with formation of **Hexahydroxybenzophenone**, $C_{13}H_{10}O_7$, when tannin is heated in aqueous solution with lead dioxide (the CO_2 liberated was estimated), holds that tannin has the formula $C_{41}H_{32}O_{25}$, and that it is probably a glucoside. It was, indeed, observed by Liebig and also by Hlasiwetz that when tannin is boiled with dilute sulphuric acid it decomposes into gallic acid and dextrin or gum (reacting with $6H_2O$), but Etti (1884) and Löwe found that tannin purified with ethyl acetate does not yield saccharine substances (dextrin, etc.). Strecker and also Feist (1912) hold that tannin contains glucose. Lloyd (1908) maintains that the tannin molecule comprises six molecules of gallic acid condensed round the hexavalent nucleus, O 

The nature and mode of condensation of the tannins varies with the nature of the vegetable organisms from which they are derived, two fundamental groups being recognised: (1) *Hydrolysable tannins*; (2) *Condensed tannins*. The former comprise esters of phenol-carboxylic acids combined with phenols, carbohydrates and polyhydric alcohols, also ethers of phenolcarboxylic acids formed either among themselves or with other hydroxy-acids (the latter are known as *depsides*), and glucosides formed by union of semi-acetals of sugars (glucose, rhamnose, etc.) with alcohols, phenols and their derivatives. All tannins of this first group have gallic acid for their fundamental component and are hydrolysed by emulsin and by tannases.

The tannins of the second group contain as fundamental component the phloroglucinol residue, which may be isolated by treating with alkali, whilst treatment with strong acids or oxidising agents or bromide yields amorphous compounds of low molecular weight (sometimes *red tannins*). One class of this group comprises tannins with a basis of phloro-glucinol (or catechol) combined with a benzene nucleus,[1] a second class including those with a basis of hydroxycinnamic acid.

Tannin is widespread in nature and occurs in abundance in the wood or bark of various plants and in oak-galls (gall-nuts), which are pathological excrescences caused by incision of the oak branches by insects.[2] To extract the tannin, the gall-nuts are ground to a coarse powder, which is treated with hot water in a battery of diffusors similar to those used for extracting beet-sugar (*see* p. 549). The crude aqueous solution of tannin thus obtained is filtered through a battery of filters and extracted, in a closed copper (or bronze) vessel fitted with a stirrer, with crude ether (aqueous or not free from alcohol). After the liquid

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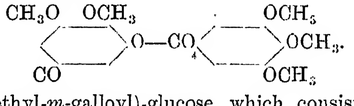
The results of the last investigations of Fischer and his pupils (1909–1919) have cast new light on the constitution of tannin. Fischer and Freudenberg (1912) hydrolysed a pure tannin and concluded that it is formed by the condensation of 5 molecules of digallic acid with 1 molecule of glucose, free carboxyl groups being absent. Indeed, Fischer prepared synthetically a compound similar to tannin and having the constitution $CH(OR) \cdot CH(OR) \cdot CH(OR) \cdot CH \cdot CH(OR) \cdot CH_2 \cdot OR$

in which the five groups R united with the glucose are formed of 5 residues of pentamethyl-*m*-digallic acid,



Hence this derivative of glucose will be a penta-(pentamethyl-*m*-galloyl)-glucose, which consists of a mixture of two stereoisomerides corresponding with α- and β-glucoses and is similar to Herzig's *methyltannin* (1905), obtained by treating natural tannin with diazomethane.

According to Procter, tannins may be classified in two fundamental groups: *catechol tannins* (those of pine, quebracho, oak, gambier, mangrove, etc.) and *pyrogallol tannins* (chestnut, sumac, myrobolan, divi-divi, valonia, gall-nuts, etc.). When distilled with zinc dust, the former yield catechol, the latter pyrogallol (sometimes phloroglucinol).

[1] In the vegetable kingdom there occur three allied groups which contain phloroglucinol, *anthocyanine*, the *flavone* colouring matters, and *phenyl styryl ketone*: all of these are derived from $\alpha\gamma$-diphenylpropane, $C_6H_5 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot C_6H_5$, and are more or less oxidised in the three carbon atom chains joining the two benzene groups, which in their turn contain hydroxyl groups in various positions.

[2] Tannin and tanning extracts are mostly obtained from the following plants:

	Per cent. of tanning substances.	Per cent. of sugar.
Oak { bark of *Quercus*	10—12	2·5—3
Oak { gall-nuts	30—35	0·7—1
Divi-divi (fruit of *Cæsalpinia coriaria*)	40—45	8—9
Sumac (leaves and branches of *Rhus coriaria* and *cotinus*)	26—30	4—5
Valonia { cupola of *Quercus ægilops* / cupola of *Quercus vallonea*	30—35	2·5—3·5
Quebracho (wood of *Schinopsis* or *Quebrachia Lorentzii*)	16—24	0·2—0·5
Myrobolans (fleshy fruit of *Myrobalanus*)	25—40	5—6
Algarovilla (beans of *Cæsalpinia brevifolia*)	40—50	8—9
Acacia { bark of *Acacia decurrens*	30—35	0·8—1
Acacia { extract of wood of *A. catechu*	45—55	—
Chestnut { wood or bark of *Castanea vesca*	8—12	—
Chestnut { extract of wood of *Castanea vesca*	20—40	2—3·5
Pine { bark of *Abies canadensis*	10—12	3—4
Pine { extract of bark	23—26	7—8
Mimosa (barks of various Australian acacias, especially *A. decurrens*, the so-called black wattle-bark)	30—45	1

has been left at rest in vats for eight to ten days, the dense lower layer containing the tannin is decanted and freed from ether by distillation. The evaporation of the water present is effected in heated, rapidly rotating drums, or on zinc plates placed in desiccators. The dry mass is then subjected to short and gentle treatment with steam—a very soft, pale, ethereal tannin being thus obtained. Tannin solutions are also concentrated under reduced pressure in multiple-effect apparatus (*see* Sugar, p. 560).

Aqueous or Alcoholic Tannin, which is extracted by water or alcohol without being purified by means of ether, is less pure.

Pure tannin forms a pale yellow light powder or sometimes crystals. It is darkened in colour by light, turns brown in the air, and dissolves in its own weight of water, double its weight of alcohol or eight times its weight of glycerol or ethyl acetate. It is almost insoluble in ether, benzene, chloroform, petroleum ether or carbon disulphide. With iron salts it forms a bluish black precipitate, and with albumin or starch a gelatinous precipitate. In aqueous solution it is dextro-rotatory ($+ 15°$ to $+ 20°$).

Tannin is used mainly, in conjunction with antimony salts, as a mordant in the dyeing of cotton with basic dyes. It is employed also in making ink and, along with gelatine, in clarifying beer and wine, forming, together with gelatine, a gummy precipitate which gradually settles and carries down with it the suspended matter of the liquid.

TANNING EXTRACTS. Powdered barks or woods are used, either before or after extraction, in tanning hides.

These *tanning extracts* [from oak bark (containing 10 to 20 per cent. of tannin), *mimosa* (30 per cent.), leaves and twigs of *sumac* (15 to 30 per cent.), *valonia* (20 to 45 per cent.), *Asiatic gall-nuts* (55 to 75 per cent.), *European gall-nuts* (25 to 30 per cent.), *divi-divi* (40 per cent.), *myrobolans* (30 per cent.), *quebracho wood* (22 per cent.), *horse-chestnut bark* (2 to 3 per cent.), *catechu* or *cutch* (40 or 50 per cent.), etc.] are now rationally prepared on an enormous scale by extracting the finely divided material with hot water in batteries of diffusors. The exhausted material is centrifuged and then burnt as fuel. From the diffusors the liquid issues at about 5° to 6° Bé. (about 6 per cent. of tanning materials), whilst the exhausted wood contains less than 2 per cent. The dilute solutions are filter-pressed, evaporated under reduced pressure in a double-effet apparatus to about 15° Bé, and then filtered hot, first through coarse and then through fine filtering cloth, the liquid being sometimes mixed with infusorial earth or bone-black so as to give a clear liquid. This is further concentrated in vacuum pans to 28° to 32° Bé. or, with extracts required to solidify when cold, to 45° Bé.

For some years these extracts have been purified and decolorised, either before or after concentration, by many different materials, but principally by sulphites, bisulphites, hydrosulphites, alkali sulphoxylates, etc.[1]

The most important extract is that of quebracho wood, which is still crudely prepared in the country of origin (Argentine), and contains about 65 per cent. of tanning material,

[1] Formerly use was made of aluminium sulphate and barium hydroxide, aluminium thiosulphate, blood albumin or blood itself, casein and soda, etc., but better results are obtained with compounds of sulphurous acid. Bisulphite renders the extracts much more soluble, as it converts part of the tannin substances into soluble sulphonic compounds, while in the resinous extract of quebracho it also causes decomposition of a glucoside present, giving the product the property of imparting a yellow colour to skins with an aniline mordant. Decoloration is, however, due more especially to the hydrosulphite either added directly (Lepetit's patent) or produced by reduction of the bisulphite added to the extract (1) by zinc or aluminium dust (Eng. Pat. 11,502 of 1902); (2) by treating the crude extract with aluminium sulphate and sodium bisulphate and then heating under pressure at 120° to 130° (U.S. Pat. 740,283); (3) by treating the extract with a mixture of formaldehyde-bisulphite and formaldehyde-sulphoxylate (Fr. Pat. 362,780); or (4) according to the recent patent of L. Dufour (Genoa), by reducing the sulphite with thiosulphate, and then with formaldehyde. Use has also been made of the waste sulphite liquors from the manufacture of cellulose (Ger. Pat. 132,224 and 152,236; U.S. Pat. 909,343, January, 1909), of aluminium amalgam (Ger. Pat. 220,021), and of chromous salts (chloride, sulphate, acetate, etc.).

An interesting method of clarifying quebracho extract and rendering it soluble even in the cold is that of A. Redlich, L. Pollak, and C. Jurenka (Ger. Pat. 212,876 of 1908): The paste deposited from the crude, cooled extract is shaken for six to seven hours with 1 part per thousand of soda at 50° to 100°, 50 litres of the red solution thus obtained being mixed with 1000 litres of the crude extract previously decanted and the whole left to stand. A flocculent deposit is thus obtained and a pale solution of pure extract which is decanted off and can be concentrated; the flocculent precipitate can be dissolved again in dilute soda and used to clarify further quantities of crude extract. Any excess of red alkaline solution may be employed for clarifying extracts of sumac, etc.

5 per cent. of non-tannins, 18 per cent. of water and 12 per cent. of insoluble matters. It is refined in European works to obtain a product poorer in phlobaphenes and more readily soluble in the cold.

The price of tanning extracts is roughly proportional to their content of tanning or tannin substances,[1] which may vary from 20 per cent. to 50 per cent., but for a given content of tannin, extracts rich in red or orange colouring-matters have the greater value; these matters are estimated in special colorimeters or in the spectroscope. A. Gansser (1909) suggested the replacement of the direct test on hide by one on strips of animalised cotton (the latter being immersed in a bath of gelatine and then in one of formaldehyde); the resultant colour on the textile is similar to that obtained on hides.

During recent years use has been made for tanning of certain artificial compounds known as *syntans*, and prepared by Stiasny (Ger. Pat. 262,558, 1913), by condensing phenolsulphonic acid with formaldehyde, or by similar means. *Neradol D*, first made by the Badische Anilin- und Soda-Fabrik, is one of these compounds; *neradol ND* is made by treating naphthalenesulphonic acid with formaldehyde, and similar products are prepared from amino- and hydroxy-naphthalenesulphonic acids. On analysis these artificial extracts correspond with an extract containing 30 per cent. of tanning material and before the war were sold at about £44 per ton. They produce a very pale tanning of the hide but give no increase in weight, so that they are used either for fine goat and sheep skins, etc., or for mixing with ordinary tanning extracts, of which they increase the solubility.

TANNING OF HIDES. The hides of oxen, horses, sheep, etc., even when freed from hair and flesh (*i.e.*, in the form of *corium*), do not keep and readily putrefy during drying or in presence of moisture. When dressed (this was carried out as early as 2000 B.C.), and, more especially, when tanned, the hides are more tenacious and resistant, do not putrefy, and do not gelatinise with boiling water, since the fibres on which the tanning material is fixed (to the extent of 30 per cent. or even more) do not agglutinate during drying, and hence remain fibrous and do not become compact and horny. The *corium* or *derma*, *i.e.*, the fibrous substance of the skin, is converted by tanning into *leather*.[2] Rational tanning

[1] *Analysis of tanning materials. See* Villavecchia's "Applied Analytical Chemistry," Vol. II., p. 331.

[2] THEORY OF TANNING. In the first half of last century, Davy, Séguin, Dumas, and Berzelius regarded the absorption of tannin by hides as a chemical reaction. In 1858 Knapp defined *leather* as an animal skin the fibres of which do not adhere during drying owing to the pores separating the fibres being filled with the tannin; tanning would hence be a simple physical phenomenon. Similar views were expressed by Reiner (1872), Heinzerling (1882), Schröder and Pässler (1892).

Th. Korner (1898–1903) also regarded it as a physical process, since neither the tanning material nor the fibres constituting the hides are electrolytically dissociated, and therefore cannot combine to form a kind of salt. Herzog, Adler, and Wislicenus (1904) also supported the physical theory.

As it has been established that the hide is capable of absorbing at its surface like a colloidal solution, Stiasny (1908) holds that tanning consists simply of a physical *absorption*, since tannin reacts with scarcely any of the known hydrolytic products of hides. Just as colouring-matters are fixed by carbon, silica, and alumina without there being any special groups to effect combination, so also in tanning all the known phenomena support the physical absorption hypothesis.

According to Stiasny, every tanning process consists in the *absorption* of a dissolved colloidal substance by the gel of the hide and in simultaneous secondary transformations (polymerisations, oxidations, etc.), to which the absorbed matter is subjected by the catalytic action of the hide, and which render the absorbed tannin insoluble and the process irreversible. This is more a physico-chemical than a physical theory.

Konnstein (Vienna) also regards the phenomenon as a physical one, owing to the absence of stoicheiometric relations.

On the other hand, Müntz (1870) and Schreiner (1890) hold that tanning must be due to a chemical phenomenon, since the same hide always absorbs the same maximum amount of a given tanning material, but Schröder and Pässler advance the objection that below the limit of maximum absorption the quantity fixed varies with the concentration of the bath, there being no stoicheiometric relations characteristic of chemical combination.

N. O. Witt (1891) maintains that leather should be regarded as a solid solution of the tanning substances in the animal fibre (the hide), in which they are more soluble than in water.

Suida, Gelmo, and Fahrion (1903–1908) revert to the chemical theory, and assert that, as tanning is preceded by treatment with acid or mordant, slight dissociation or hydrolysis may occur (as is the case in the dyeing of wool). Further, hide powder fixes substantive dyes better than wool itself, and that the combination does not exhibit stoicheiometric proportions is explained by the fact that the hide consists of compact fibres and not of separate molecules as in solution, so that the tanning liquor penetrates only slowly into the interior of the mass, and is gradually impoverished and exhausted.

Fahrion (1908–1919) points out that in tanning with formaldehyde there can be no question

was introduced only when the anatomical structure of the skin became exactly known and the effects of tanning materials on the different parts of the hide were studied.

A clean cut in a fresh ox-hide shows the following layers: the thin exterior layer of *epidermis* or *cuticle* (Fig. 447); the thicker layer *l* immediately below is the *corium* or *derma*, which constitutes the leather after tanning; below the corium is the fatty layer *f*.

In the unhairing of the hide, the hairs and also the epidermis are removed, the corium being exposed with a papillary surface covered with a fine membrane, *p*, surrounding the hair-orifices and giving the natural lustre of the tanned hide; its sinuosities form the so-called natural *grain*, which serves to distinguish the hides of different animals. The dry hide contains 50 per cent. C, 25 per cent. O, 7 per cent. H, 17·8 per cent. N and traces of mineral matter.

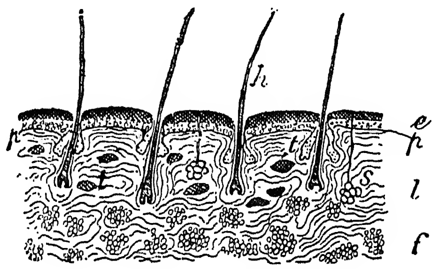


Fig. 447.

Various methods of tanning are in use: (*a*) **Mineral Tanning** or *tawing*, by means of alum and sodium chloride; (*b*) **Oil Tanning** or *chamoising*, with fatty materials; (*c*) **Ordinary Tanning** with tannin substances; (*d*) **Chrome Tanning**, using chromium salts (tanning with formaldehyde, proposed by Trillat and Payne; with quinone by Meunier and Seyewetz; with naphthols by Weinschenck; with rare earths by Garelli; with fatty acids by Knapp, or with the corresponding ammonium soaps by Garelli and Corridi, 1909).

Garelli (1914) obtained a pseudo-tanning with bismuth nitrate, mannitol (or glycerol) being added to prevent separation of basic compounds. Apostolo (1914) showed that hides may absorb suspended substances and effected pseudo-tanning with precipitated sulphur (or fats). Knapp obtained distinct tanning with fatty acids.

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of colloidal material (as with tannin), and with regard to the elimination of alum or tannin from leather by the mere action of water, this is due to *pseudo-tanning*, *i.e.*, to the formation of labile, readily hydrolysable compounds, the tannin of which becomes distributed between the hide and the water. With reference to the non-stoicheiometric relations, he observes that the fixation of more tannin from concentrated than from dilute solutions is in accord with the law of mass action for reversible chemical reactions.

According to Heidenhain, Zacharias, and Fahrion (1908), both the dyeing and the tanning processes occur in two phases, the absorption and penetration of the tanning substance and the subsequent chemical combination of this substance with the hide. Garelli (1907–1910), from the results of his tanning experiments with rare earths (ceria, thoria, zirconia), supports this theory, and holds that all substances which in aqueous solution can undergo hydrolysis forming basic hydroxides or salts (like chromium, iron, and aluminium salts) are capable of tanning hides (*i.e.*, the hide hydrolyses and decomposes the salts, which thus deposit hydrates or basic salts on the fibres of the *corium* or *derma*, the fibres and the salts combining to form leather). Thus, Garelli effected tanning with the rare earths, *i.e.*, with compounds of the trivalent (cerium, lanthanum, and didymium) or tetravalent elements (cerium, thorium, and zirconium; Zacharias had used stannic salts in 1903), and the tanning, as when alum is used, is facilitated by sodium chloride (this was not used with ceric salts, which would generate chlorine). The most effective tannings are those in which an oxidation plays a part (the metals pass from the higher to the lower valency) and those with alum, which cannot give salts of lower valency but are not very stable, and do not resist even the prolonged action of cold water (*pseudo-tanning*). Chromium salts are reduced to oxides by the skin and fixed, while oils and fats must be oxidised (to hydroxy-acids), as otherwise the tanning is not complete.

R. Lepetit (*Ann. d. Soc. chim. di Milano*, 1907, p. 83) asserts that in the tanning of sole and upper leather it is not sufficient to effect separation and stabilisation of the fibres, but that it is necessary to produce swelling and filling of the interstices between the fibres with *phlobaphenes*. These are colloidal substances dissolved or suspended in the tannin extracts and consisting partly of internal anhydrides of soluble tannins (*see* p. 687) and partly of condensation products of formaldehyde with polyphenols and phenolcarboxylic acids derived from the tanning vegetable organisms. Indeed, according to Nierenstein, the products of the reaction between formalin and polyphenols exhibit tanning properties, and at the present time glove leather is successfully tanned by formaldehyde (Trillat and Payne). Also Weinschenck (1907–1908) stated that α- and β-naphthols in presence of formaldehyde are able to tan hides, but this is denied by Stiasny and Ricevuto (1908). In tanning with quinone derivatives (suggested by Meunier and Seyewetz) leather is formed, owing to the hydroquinone derived from the quinone reacting with the amino-groups of the proteins. With formaldehyde, there is probably production by aldol condensation, of complex colloidal polymerides of formaldehyde (especially in presence of alkali carbonate), these reacting with aminic complexes in the same way as formaldehyde and the aldols react with aniline (*see* p. 659). Thuan (1909) found that if the hides are previously treated with formaldehyde subsequent chrome tanning is hastened.

The tanning power of the various materials used in practice may be established roughly by determining the temperature of gelatinisation or shrivelling of the strips of tanned hide when heated with water, the best tanned hides showing the highest temperature. If the gelatinising temperature of the best chrome tanned hides is taken as 100, those for other tanning will be: quinone tanning, 100; chamoisine, 85 to 90; formaldehyde tanning, 85 to 90; neradol tanning, 80 to 86; 70 for vegetable tanning; 58 to 60 for fatty acid and resin tanning, and 50 for alum tanning.

Various bacteria, even injurious ones, develop on insufficiently dried or fresh hides. The ordinary antiseptics (phenols, formaldehyde, etc., which have tanning action) cannot be employed, and the most convenient treatment is with dilute formic acid, or 0·1 per cent. sodium hydroxide, or 0·2 per cent. sodium sulphide solution at 18°. The fresh hides as they come from the slaughterers are termed *green hides*, and in this condition an ox hide will weigh from 30 to 40 kilos, its weight being reduced to one half by tanning. Many hides are imported from South America in the dried and salted or smoked state. Ox hides give the heaviest leather for boot soles, while for lighter soles cow hide is used; the uppers are made preferably from calf skin. Saddles are made from horse hide, pig skin, and seal-skin, while sheep-skin is used for bookbinding leather and goat skin for morocco leather. Deer-skin, goat-skin, etc., are tanned with oil to obtain chamois or buff leather (*see later*).

The hides are first *softened* by soaking for two days or longer (according as they are

FIG. 448.

FIG. 449.

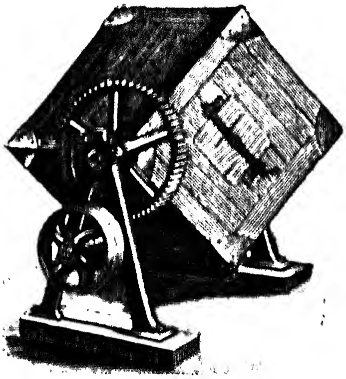

FIG. 450.

green or dry) in soft water, which removes blood and other adherent impurities. This may be accelerated, especially with large and dry hides, by adding about 3 kilos of crystallised sodium sulphide or 1 kilo of caustic soda per cu. metre of water. The hides are then placed on a "beam" (Fig. 448) and scraped on the flesh side with a curved knife (Fig. 449), which is drawn across them horizontally. They are then soaked for 24 hours, scraped again, washed in water for a few hours, thrown on the beam and allowed to drain. This operation is hastened if the softened hides are subjected to fulling in a revolving vessel (Fig. 450) or in a vat containing cold water in which they are worked with wooden mallets.

In order to remove the hair fixed in the epidermis (not in the corium), the epidermis must be attacked and almost destroyed, this being effected in various ways (by putrefaction, lime, or sulphides). Putrefaction ("sweating") is carried out by salting the flesh side of the hides or sprinkling them with crude acetic acid, bending the hides in two longitudinally with the hair outside and stacking them in tanks or in a warm chamber (30° to 50°); fermentation soon sets in, accompanied by heating and evolution of ammonia, the hides being then unhaired on the beam with a suitable knife. In order to avoid the possibility of excessive heating, the hides are sometimes placed in cement troughs fitted with perforated, wooden, false bottoms, water being sprayed on to the hides at the top, so that the temperature is kept down to 10° to 12°; after 8 to 12 days the hides can be readily unhaired. The more delicate skins of small animals are treated with sulphides, being smeared with *rusma*, which consists of a mixture of 1 part of arsenic sulphide (orpiment) with 2 to 3 parts of slaked lime; calcium hydrosulphide is also used and gives better results. In recent years, sodium sulphide has also been used for heavy hides, unhairing being easily carried out by scraping the hides (after washing) with a knife against the set of

the hair, the operation being facilitated, if necessary, by sprinkling a little sand or ashes on the hide; the hair serves for the manufacture of felt, but that treated with sulphide is converted into fertiliser.

In large tanneries unhairing is effected by means of machines (Fig. 451), in which the hides are spread on three or four vertical plates and pressed against revolving rollers with helical knives inclined in two directions. The hides are then washed in a large quantity of water, spread out and beaten on the beam, and the defleshing of the under side completed either with a curved knife or in the machine shown in Fig. 452; the flesh removed is mixed with lime and sold for making glue. In many factories large hides are rendered uniformly thick and then split into 3 to 6 sheets, sometimes only a fraction of a millimetre in thickness, by means of a moving, endless knife; a band knife splitting machine is shown in Fig. 453.

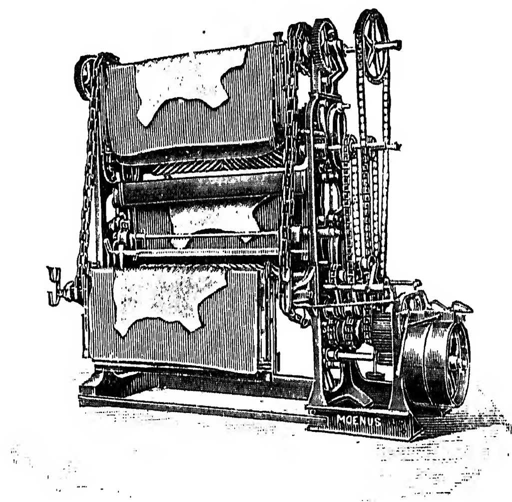

FIG. 451.

The hides are often further defatted either by pressing or, better, by means of a solvent such as benzine or trichloroethylene, the fat being recovered and used for soap-making. In order to preserve the hides if they are not to be tanned immediately, or to prepare them for chrome tanning, they are *pickled* by immersion for about an hour in a bath containing 7·5 grms. of H_2SO_4 and 80 grms. of NaCl per litre; the acid is rapidly absorbed, and the salt prevents excessive swelling. They are then rinsed in saturated salt solution and, after draining, may be made up into bales. To eliminate the pickling prior to tanning, the hides are washed in a salt bath containing borax. Pickled hides yield a pasty leather and require less tanning material.

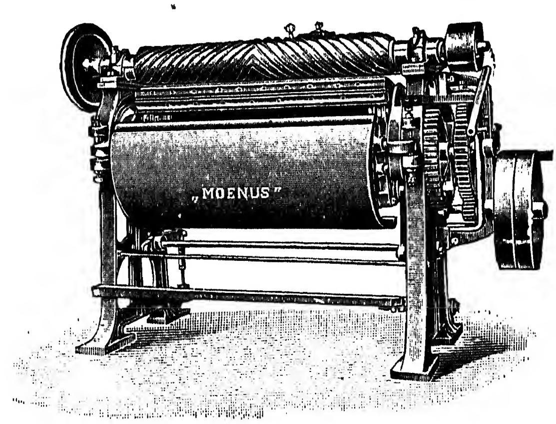

FIG. 452.

The hides have by this time lost about 12 per cent. in weight, and those which have been limed are next kept for two or three days in several successive infusions of barley flour or bran ("bran drench") in active acid fermentation; to these are added sulphurous or sulphuric acid, lactic acid (or better, according to Boehringer, Ger. Pat. 234,584 of 1909, a solution of lactic anhydride in ammonium lactate), or acetic or butyric acid, the calcium soaps on the hides being thus decomposed; the acids separate at the surface and the soluble calcium salts are eliminated by washing (at one time, mixtures of dog and bird dung with water were used, the action of these being due to enzymes and amine hydrochlorides; these enzymes, however, act on the gelatine of the hide, this being eliminated, together with the lime, by washing with tepid water). The dung is now preferably replaced by various selected bacterial cultures and enzyme preparations. After a few days the hides swell up to double their original size and become yellowish and transparent. Excessive swelling is prevented by the addition of a little tanning material to the infusion.

All these preparatory operations are required to make the material to be tanned more

permeable and more uniform in its behaviour towards the tanning agents, which are fixed to the extent of about 30 per cent. (calculated on the dry corium). The tanning can now be carried out by the following methods:

(*a*) *Infusion tanning.* This process, which is used for lighter hides, consists in passing the hides into tanning baths of gradually increasing strength, so that the tanning may be gradual and penetrative. The total time required is 6 to 9 weeks, and between each

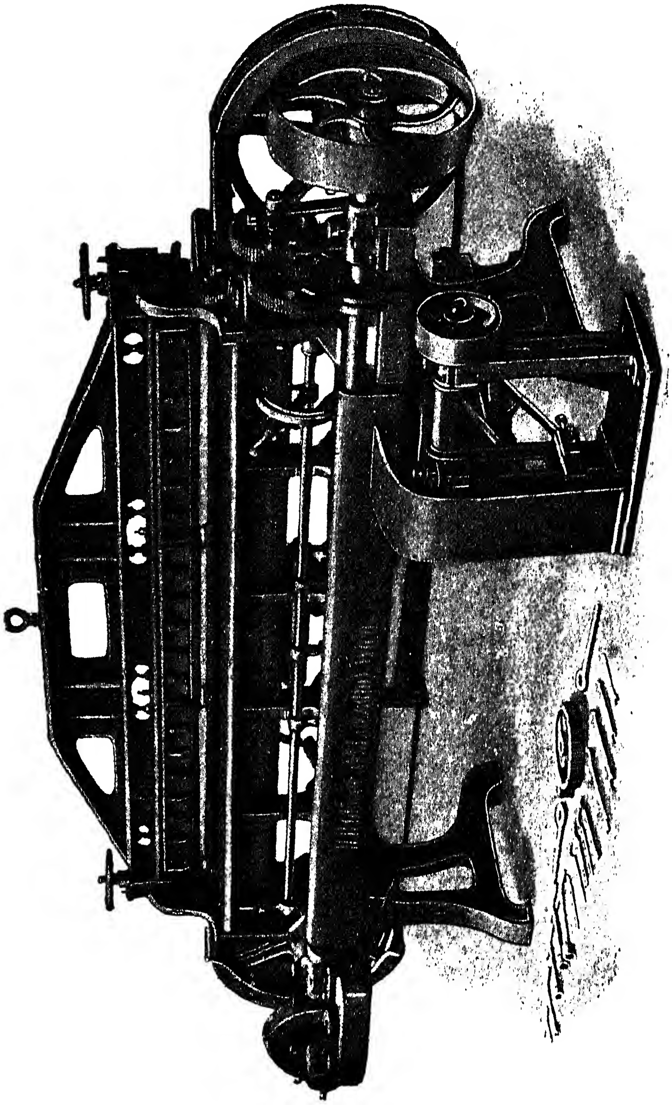

FIG. 453.

bath and the succeeding one the hides are drained, pressed, and fulled in order to facilitate the absorption of the tannin.

(*b*) *Tanning in layers* was once largely used but is now employed more particularly for sole leather. Fifty or sixty hides are placed, alternately with layers of powdered or crushed tanning material (bark, wood, etc.), in a cement or wooden vessel, the empty spaces being then filled with the tanning material and the whole covered with water. The vessel is then closed with an air-tight cover and left for about 2 months, the hides being then transferred to a second similar vessel containing rather less tanning material, where they are left for 3 to 4 months, and finally to a third vessel containing still less tanning material (4 to 5 months).

If the hides are very heavy and resistant, they are passed to a fourth and sometimes to a fifth bath or pit, the whole operation then occupying about two years and the consumption of bark being about five times the weight of the dry hides. The completion of the tanning is ascertained by cutting the hide and observing that the section is uniform and without horny or fleshy layers, and that the grain does not crack when the hide is carefully bent.[1]

(c) *Rapid tanning*, which gives a greater output of leather, has been attempted in many different ways: By immersing and compressing the hides in relatively concentrated tanning baths prepared from active, modern extracts, and containing a certain amount of acid to prevent wrinkling of the hides, the tanning liquor being circulated by means of pumps without moving the hides; or the skins are placed in revolving barrels or drums, the lower half dipping into tanning liquor so that the hides are pressed at intervals. The diffusion process is also applied by placing the tanning bath in bags composed of various hides sewn together. Tanning in a vacuum has likewise been used in order to effect better penetration of the tanning material, considerable pressure being exerted automatically on the hides at regular intervals, and the operation being facilitated by gentle heat, etc. By these rapid processes (*see also* Use of Quinone, Ger. Pat. 206,957, 1907) tanning can be completed in 6 to 8 weeks, this including the preliminary preparation of the hides. The actual

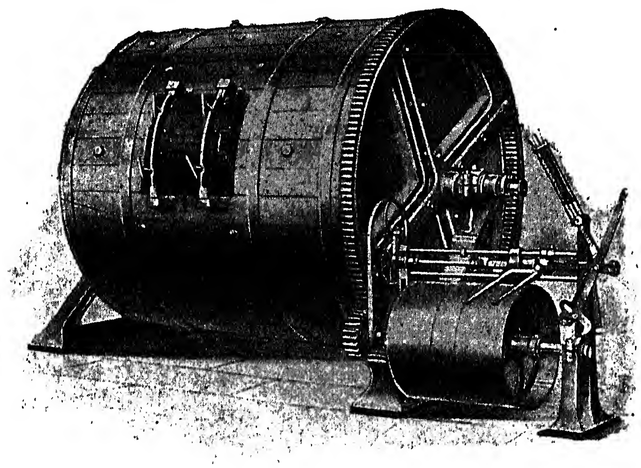

FIG. 454.

tanning may, indeed, be limited to 30 hours if revolving barrels are used with hot, highly concentrated tanning baths (8° to 10° Bé.). When such a rapid process is used it is, however, indispensable to eliminate all traces of lime beforehand by immersion in formic acid solution. Other very rapid methods which are largely used are chrome tanning (*see above*) and formaldehyde tanning as proposed by Payne.

According to Gilardini (Fr. Pat. 485,044, 1917) instantaneous tanning may be effected by passing concentrated tanning extracts (25° to 30° Bé.) under pressure through the hide rolled on a perforated drum, the outside space being evacuated. The best results are, however, obtained with the artificial tannins, neradol D and ND.

Accelerated tanning is facilitated by the mechanical action of periodic compression of the hides in rotating chests (Fig. 450) or drums (Fig. 454). When the drum rotates the hides are lifted to a certain height by means of pegs and then allowed to fall forcibly into the tanning solution and on to the hides in it.

(1) Mineral Tanning or *tawing* is frequently used for light lamb, sheep, and goat skins, which, after unhairing, are passed into the limes and are then, just as in ordinary tanning, swelled in an acid bath, which also removes all the lime. They are then placed in the

[1] F. Carini (*Ann. d. Soc. chim. di Milano*, 1903, p. 23, and 1904, p. 144) proposes to use the hydrostatic balance in order to obtain the weight of the dry hide from that of the wet hide, without drying. The hides can thus be followed through all the operations, from their entry in a more or less moist state. The quantity of tanning material fixed can also be determined at any moment in this way.

tanning vat containing alum or sodium chloride solution, without impregnating them with fatty substances. For twenty hides, about 1500 grms. of alum and 500 grms. of sodium chloride are dissolved in 50 litres of tepid water. The hides are well saturated with this bath and are heaped up still wet for two or three days, after which they are pressed, washed, and allowed to dry in the air.

The finishing of the tanned hides is carried out as described later.

Mineral tanning is usually a rapid process, and the alum combines with the corium and preserves it, but the leather is not so lasting as that prepared with tannin and can still be gelatinised by prolonged boiling with water. A highly elastic leather is, however, obtained.

Chromium salts (the alum and chloride) are often used nowadays in place of alum and sodium chloride.

(2) **Chrome Tanning** has assumed considerable importance of recent years (since 1895), as it is rapid and furnishes boot leather highly resistant to wet; it is often used also for girths, etc. Both alum and chrome tanning give a light, soft and tenacious leather, chrome tanned leather being far more resistant to boiling water and to tension than vegetable tanned leather.

With chrome tanning the hide fixes only 3 to 4 per cent. of chromium oxide, the latter being hence sold by measure instead of weight. If dried the leather cannot be swollen, so that it is dyed and dressed immediately. This mode of tanning may be carried out in either a single bath or in two baths at 25° to 30°. In the first case the hides are immersed directly in a solution of a basic chromium salt, whilst in the second they are first soaked in chromic acid solution (potassium or sodium bichromate with sulphuric or hydrochloric acid), then rinsed and placed in a second bath containing a reducing substance (best sodium thiosulphate, although sodium sulphite or bisulphite, arsenious acid, hydrogen peroxide, nitrous acid, etc., are also used).

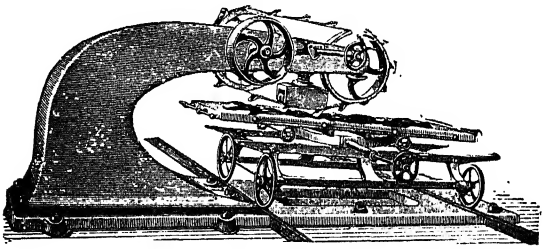

FIG. 455.

(*a*) *Single Bath.* The basic chromium salt is obtained either by treating chrome alum with sufficient soda to give the desired basicity, corresponding, for example, with the formula, $Cr_2(OH)_2(SO_4)_2$, or from potassium bichromate, an acid and a reducing agent.[1] The completion of the tanning is determined by examining a clean cut made in the thickest part of hide or by the absence of wrinkling when a piece is placed for a few minutes in boiling water.

(*b*) *Two Baths.* The first bath may contain 1000 litres of water, 10 kilos of bichromate and 5 kilos of hydrochloric acid per 250 kilos of hides, less acid being used with pickled hides; more bichromate is often used. For this bath vats with reels or the revolving drums may be employed, the hides being treated until they are coloured yellow throughout, then left to drain for some hours in the dark, and then immersed in drums containing the second, reducing bath. This may contain 1000 litres of water, 25 kilos of thiosulphate and 13 kilos of hydrochloric acid per 250 kilos of hides. The treatment in this bath lasts some hours or at most a day. The sulphur which always separates is partly absorbed directly by the hides and partly transforms the thiosulphate into tetra- and penta-thionate. When, as is now more commonly the case, a single bath is used, this contains *chromo-base*, which is a basic sulphate prepared by the firm of Lepetit, Dollfuss, and Gansser; the procedure is as in the preceding case. The use of chromium lactate has been recommended, since lactic acid reduces chromium salts, even in the cold.

(3) **Oil Tanning** or *chamoising.* This is used to obtain very soft leather for gloves, clothing, etc. Deer, stag, lamb, kid skins, etc., are smeared or rubbed with various fats [fish oil, wool fat, paraffin, egg-yolk, alum, carbolic acid, sodium chloride, etc.; or, according to Garelli and Apostolo (1914) with stearic, palmitic, oleic acids, etc., or resin acids such

[1] The basic chromium salt is formed as follows:

$$Cr_2(SO_4)_3, K_2SO_4, 24H_2O + Na_2CO_3 = Cr_2(OH)_2(SO_4)_2 + K_2SO_4 + Na_2SO_4 + CO_2 + 23H_2O,$$
or
$$K_2Cr_2O_7 + 3H_2SO_4 + 3Na_2S_2O_3, 5H_2O = K_2SO_4 + Cr_2(OH)_2(SO_4)_2 + 7H_2O + 3Na_2SO_4 + 3S.$$

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as those from colophony, or, better, according to Fahrion, with unsaturated fatty acids with several double linkings], the absorption of which is effected by repeated working of the skins, followed by drying in tepid chambers; the skins are thus rendered impermeable, while they can be washed many times without losing their tanning. The superficial fat is finally removed by washing in soda solution, the emulsion thus formed, known as *dégras* (*see* p. 478) being used for currying ordinary hides.

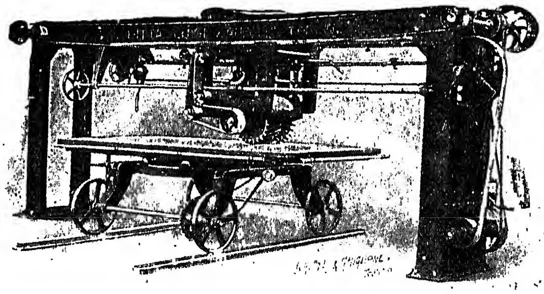

Fig. 456.

Heavier hides (cow, horse, ox, buffalo) intended for saddlery are subjected to mineral tanning (without being treated with lime) and afterwards to a kind of oil tanning which imparts to the leather considerable resistance to tension.

The tanned hides are then subjected to *finishing*, which varies considerably with the nature of the hide and the kind of leather required.

(*a*) *Smoothing and Stretching.* The tanned, moist hide is stretched on a plate moving on wheels mounted on a trolley so as to give both longitudinal and transverse movements, the machine being known as a striking-out and scouring machine (Fig. 455). A band moving over two pulleys is furnished with inclined blades of bronze, ebonite, glass, etc., these impinging more or less strongly on the bloom side of the hide and so squeezing out the water and smoothing out the folds. A better machine for this purpose is shown in Fig. 456; in this, the hide is pressed and stretched by a bronze cylinder having doubly inclined helical vanes. Machines similar to those used for defleshing (Fig. 452) are also employed.

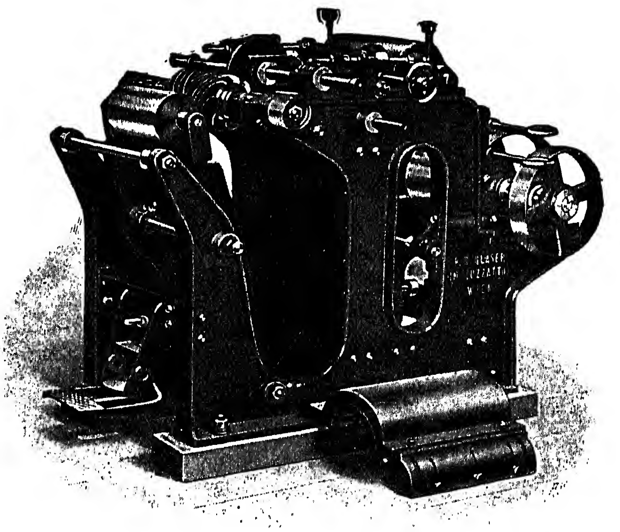

Fig. 457.

(*b*) In order to prevent cracking or splitting during drying, the hides are subjected to slight *oiling*, with fish oil, linseed oil, castor oil, lanoline, *dégras*, egg-yolk, tallow, stearine, paraffin wax, etc., according to the type of hide and to the rigidity or softness required.

(*c*) *Shaving* generally follows, this consisting in stretching the hide on a rubber cylinder (Fig. 457), which presses it against a second cylinder furnished with helical blades, one-half of these sloping one way and the rest the other way.

(*d*) *Drying* of the hides is carried out carefully in circulating air, which is dry rather than warm and does not effect complete drying.

(*e*) To render the almost dry hides less stiff and softer, adherent and hardened fibres are detached by bending and pulling out hides in all directions; this is usually effected mechanically.

(*f*) To render sole leather more compact and more resistant to wear, the hides are subjected to *striking* by means of a bronze piston operated by a lever (Fig. 458); excessive striking marks the leather. A preferable method consists in *rolling* by means of a weighted roller moved backwards and forwards by means of an endless screw (Fig. 459).

(*g*) Many skins are *glazed*, and to obtain a good, resistant lustre they should be free from fat and dry. If too greasy they are rubbed with 5 per cent. lactic acid or ammonia solution. When dry they are rubbed with a very thin layer of a special dressing (aqueous egg albumin and milk, and other pale dressings known as *seasoning*), the rubbing being effected by a smooth agate or glass cylinder.

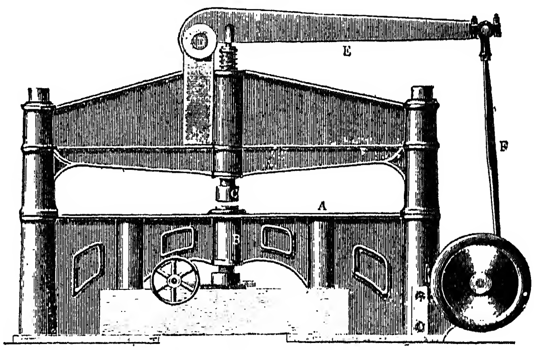

Fig. 458.

(*h*) If this cylinder is finely grooved the leather assumes a rough, fine-grained surface, which may be rendered more marked (morocco leather) either by bending the hide over on itself and rubbing the surface gently with a cork utensil (Fig. 460), or by passing the hide between two rollers revolving at different speeds. More pronounced impressions to give the appearance of goat, seal, crocodile skins, etc., are obtained by means of calenders suitably incised, the upper roller being heated to render the impression more stable.

Those hides which are required to show not graining but a smooth surface, are first rendered perfectly uniform at the surface by rubbing both sides with pumice by hand or more conveniently by a kind of spindle-shaped grindstone covered with emery (Fig. 461), against which the surface of the hide is gently pressed. In some cases this operation is completed by polishing the bloom side with a concave piece of wood, similar to that of Fig. 460, but with a smooth surface lined with cork.

(*i*) Certain hides and leathers are rendered *waterproof* by immersing them for a couple of hours in baths of soap and glue and then in aqueous alum and salt solutions. Good results are obtained also with 2 per cent. gelatine solution, followed by 5 per cent. formalin. *Hardened leather* for boot soles is treated with 2 per cent. formalin for 24 to 48 hours, chrome-tanned leather being subjected also to a bath containing 8 per cent. of aluminium sulphate and 1 per cent. of sulphuric acid.

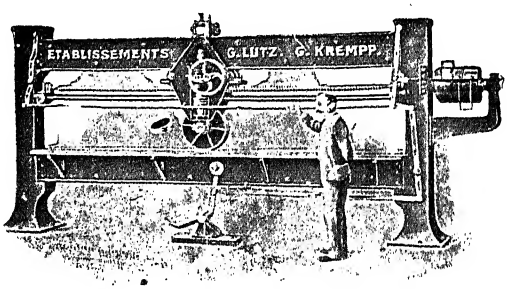

Fig. 459.

(*k*) Some hides are dressed to increase their weight with starchy substances or dextrin (brillantine, containing over 60 per cent. of dextrin, 9 per cent. of soluble starch, 5 per cent. of maltose, and 25 per cent. of water) in strong solution, with which they are treated for a couple of hours in drums; the increase is greater if magnesium sulphate or barium chloride is used. Hides are loaded also with excess of tanning agent, oils and fats, sulphite liquors from cellulose factories, glucose, barium sulphate, magnesium sulphate, etc.

(*l*) Bleaching and dyeing of hides are carried out by the varied processes used for textile fibres, especially animal fibres (wool and silk). For *bleaching*, which prepares the hides for taking the paler tints, use is made of hydrogen peroxide, sulphurous acid, sulphites, oxalic acid, permanganate followed by sodium bisulphite, dilute hypochlorite, etc. *Dyeing* of vegetable or alum tanned hide is effected at 40°, and that of chrome tanned ones at 60°.

Leather for boot uppers is coloured black on the flesh side by rubbing with concentrated solutions of iron acetate and sulphate, treating with oil, wax, soap, lampblack, etc., and then polishing with smooth wood until a shining surface is obtained.

For special purposes hides and leathers are coloured with basic or mordant aniline colours, the hides being first prepared by immersion for 12 hours in cold water in which is dissolved the white of an egg for each hide. The dyeing is carried out at a temperature of 30°. Certain leathers are varnished with ordinary resin varnishes. In order to supply the great demand for large hides for the hoods, etc., of carriages, ox-hides and cow-hides are nowadays divided, the more resistant part being kept for the hoods, and the flesh side for the seats, etc.

FIG. 460.

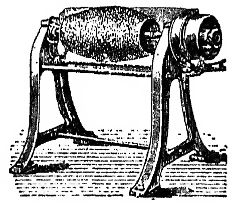

FIG. 461.

In order to avoid the formation of the white efflorescence—caused by the use of hard water and due to the combination of lime with the fatty matters of the tanning materials—it has been proposed to replace the fats by mineral oils, which do not give calcium salts, or to wash the hides well with dilute lactic or formic acid which form soluble calcium salts. The suggestion has also been made that the hides be dressed, not with fats, but with the anhydrides or lactones of fatty acids, as these form calcium salts more slowly (the *purgatol* recently placed on the market consists mainly of anhydrides or lactones).

M. NITRO-DERIVATIVES OF BENZOIC ACIDS

o-**Nitrobenzoic acid** melts at 147°, has a sweetish taste and at 16° dissolves in 164 parts of water. The *m*-**Acid**, m.-pt. 141°, dissolves in 425 parts of water at 16° and yields a sparingly soluble barium salt. The *p*-**Acid**, m.-pt. 238°, is very slightly soluble in water.

2 : 4-**Dinitrobenzoic acid** (*see* p. 652) has m.-pt. 179° ; the 2 : 5-**Acid**, m.-pt. 177° the 2 : 6-**Acid**, m.-pt. 202° ; the 3 : 4-**Acid**, m.-pt. 165°.

2 : 4 : 6-**Trinitrobenzoic acid** melts at 210° losing CO_2 and yielding *s*-trinitrobenzene (*see* p. 649). Its use as an explosive was proposed by the Griesheim-Elektron Company (Ger. Pat. 79,314, 1893).

Numerous halogenated derivatives of the nitrobenzoic acids are known.

N. HYDROGENATED BENZENE COMPOUNDS

Considerable interest attaches to the numerous *hydrophthalic acids* studied by Baeyer in their various constitutional and stereo-isomerides (*cis*- and *trans*-isomerides : *see* p. 22).

They behave largely like unsaturated aliphatic compounds (*see* pp. 106—108), as they no longer possess the stability of the true benzene nucleus. The position of the true double linkings in these compounds is determined by the addition of bromine and by subsequent elimination of the latter by reduction, with or without substitution of hydrogen, according as the two bromine atoms are in para- or ortho-positions. Simple boiling with alkali often effects displacement of a double bond (as with oleic acid ; *see* p. 358), so that it is possible to pass from one isomeride to another.

The di-, tetra, and hexa-hydrophthalic and terephthalic acids can be dehydrogenated in stages by heating with bromine at 200° ; many of them form anhydrides.

From the results of his investigations on the hydrophthalic acids Baeyer drew important conclusions concerning the constitution of the benzene nucleus.

Many important hydrogenated benzene derivatives occur naturally, among them the *naphthenes*, found in abundance in Russian petroleum (*see* p. 71), which contain hexamethylene groupings (*see* Polymethylenes, p. 616). Synthetically they may be obtained, for example, from calcium pimelate :

$$CH_2<\begin{matrix}CH_2\cdot CH_2\cdot CO_2\\ CH_2\cdot CH_2\cdot CO_2\end{matrix}>Ca = CaCO_3 + CH_2<\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}>CO \text{ (\textit{ketohexamethylene})}.$$

Also, by condensing 2 mols. of ethyl succinate with sodium and then hydrolysing the product and heating at 200°, *p-diketohexamethylene* is obtained. Hydrogenation of benzene and its homologues, by passing their vapours, mixed with hydrogen, over heated finely divided nickel, yields *hexamethylene* [1] and its homologues, *hexahydrophenol* (b.-pt. 160·5°), and *p-diketohexamethylene* (m.-pt. 78°). The latter gives the corresponding alcohol, *quinitol* (*p-dihydroxyhexamethylene*), which forms various *cis-* and *trans*-isomerides. *Inositol*, $C_6H_{12}O_6$, the hexahydric alcohol derived from hexamethylene, is isomeric with the hexoses, but with HI or PCl_5 yields true benzene derivatives.

Various *naphthenic acids* are obtained by oxidation of the naphthenes of Russian petroleum, or more easily by acidifying the alkaline solutions used in refining this petroleum (*see* pp. 79, 89), and are distinguished from open-chain acids by forming soluble magnesium and calcium salts ; by this means they can be detected when used in the manufacture of soaps.[2] Charitschkov (1911) showed that these acids are not of the hexamethylenecarboxylic acid group, since the latter acid melts at a higher temperature and does not give the characteristic reaction with copper or cobalt salts obtained with naphthenic acids. The latter resemble rather **Pentamethylenecarboxylic acid**, $CO_2H \cdot CH\left<\begin{matrix} CH_2 \cdot CH_2 \\ \quad\quad | \\ CH_2 \cdot CH_2 \end{matrix}\right.$, and Zelinsky's **Pentamethyleneacetic acid**, $CO_2H \cdot CH_2 \cdot CH\left<\begin{matrix} CH_2 \cdot CH_2 \\ \quad\quad | \\ CH_2 \cdot CH_2 \end{matrix}\right.$, which give the reactions mentioned. Naphthenic acids are optically inactive and insoluble in water, and boil unchanged. The first terms are mobile liquids of unpleasant odour, which disappear as the molecular weight increases ; the higher members are viscous but of lower density (0·98 to 0·95).

QUINIC ACID (**Tetrahydroxyhexahydrobenzoic acid**), $CO_2H \cdot C_6H_7(OH)_4$, is optically active, but only an inactive modification is known. It is obtained from the roots of coffee, cinchona, etc., and forms white crystals.

Still more interesting are the *terpenes* and the *camphors*, which are found in various plants and form the principal constituents of many *ethereal oils* and *essences* and of many *resins*.

TERPENES

These are regarded chemically as hydrogenated derivatives of cymene (dihydrocymene) and its homologues, and have the generic formula $C_{10}H_{16}$. They are not soluble in water, but can be readily isolated from the natural products owing to their volatility in steam.

The chemical constitutions of the principal terpenes have been established mainly by O. Wallach's investigations over a period of more than twenty years. By their syntheses, their halogenated additive compounds, their behaviour towards oxidising agents and their molecular refraction (*see* p. 27), it has been shown that they contain two double linkings and a closed ring of six carbon atoms.

There is, however, a group of more complex terpenes (pinene, camphene, fenchene, etc.), which have only one double bond. In order to define the position of the double linkages (Δ), Baeyer numbered the fundamental carbon atoms

[1] **HEXAMETHYLENE** (*hexahydrobenzene*, *cyclohexane*, or *naphthene*) is found in Caucasian petroleums and is obtained synthetically from iodohexamethylene or 1 : 3-dibromopropane. It is a colourless liquid smelling like petroleum, and it boils at 80° and resists the action of permanganate. By hydriodic acid at 750°, or in presence of alumina at lower temperatures and preferably under pressure, it is converted into methylpentamethylene.

[2] Naphthenic acids serve for the regeneration of rubber, for preserving wood in virtue of their antiseptic properties, and for making alkaline soaps of marked detergent power ; the aluminium salt is used for impregnating wood, and the manganese and lead salts as dryers for oils ; the corresponding glyceride is used as a lubricant, as a tanning agent, etc.

of the cymene as in the first figure of the following scheme, which shows the constitution of five *terpadienes* out of fourteen possible theoretically without counting enantiomorphs.

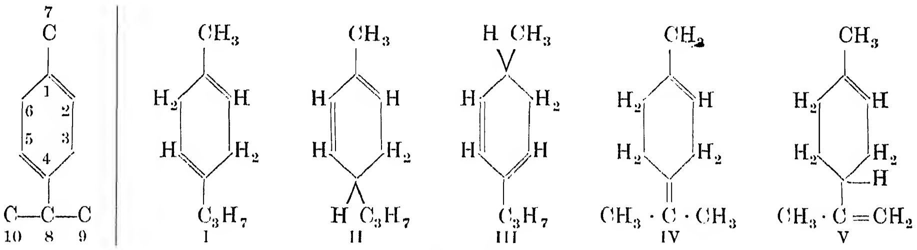

FIG. 462.

To indicate the position of the double linking in the side-chain, instead of giving only the lower number of the two carbon atoms united to the double linking, as in the case of the nucleus (*e.g.*, III = $\Delta^{3,5}$-terpadiene ; II = $\Delta^{1,5}$ terpadiene or *a-phellandrene* ; I = $\Delta^{1,4}$-terpadiene or γ-terpinene), the numbers of both the carbon atoms united to the double linking are given, the higher number being bracketed (*e.g.*, IV = $\Delta^{1,4(8)}$-terpadiene or *terpinolene* ; V = $\Delta^{1,8(9)}$-terpadiene or *limonene*). In the official nomenclature the name *terpane* is given to **Hexahydrocymene**, $C_{10}H_{20}$, **Tetrahydrocymene**, $C_{10}H_{18}$, being called *terpene* and the **Dihydrocymenes**, $C_{10}H_{16}$, *terpadienes*.

As separated from plants or fruits, the terpenes are generally mixtures, and when obtained from conifers are termed *oil of turpentine*. Essence of lemon gives *citrene* ; thyme, *thymene* ; cumin, *carvene* ; orange, *hesperidine*, etc. Although their boiling-points differ little (160° to 180°), they form tetrabromo-derivatives and dihydrochlorides with widely different melting-points, these compounds hence serving for their separation.

PROPERTIES. Owing to the presence of double linkings, which act as in aliphatic compounds, the terpenes can combine with 4 bromine atoms or 2 mols. of HCl (the halogen being readily replaced by hydroxyl, with formation of camphor) and also react with nitrous acid or nitrosyl chloride, forming solid **Nitrosites**, $C_{10}H_{16}(NO_2)(NO)$, or **Nitrosochlorides**, $C_{10}H_{16}(NO)Cl$, which are also solid and sometimes blue.

They oxidise easily and with mild oxidising agents give benzene derivatives, whilst on energetic oxidation they resinify ; they polymerise readily, and by acids, for instance, are converted into more stable isomerides. In alcoholic solution they give characteristic colorations with concentrated sulphuric acid. They are usually optically active.

They often accompany the *natural perfumes* of fruits and flowers, which, now that they have been subjected to thorough chemical study, can be obtained purer and of increased value.[1]

[1] **PERFUME INDUSTRY.** A considerable number of the *natural perfumes* have been prepared from the very earliest times, but with the perfected methods of extraction now available they are obtained in higher yields and in a more highly refined condition. The most abundant supplies of raw material have always been, and are still, obtained from eastern countries, where whole provinces are often devoted to the cultivation of flowers.

The most delicate perfumes are those obtained from flowers which contain, along with the odorous principle, other substances which refine the aroma and render it softer. The name artificial perfumes was at one time given to mixtures, in proportions carefully chosen, of the fundamental natural essences, a great variety of perfumes being thus obtained ; this, however, required a very highly developed sense of smell in the operator.

The discovery of artificial perfumes did not diminish the consumption of the natural products since these became cheaper and thus appealed to a large public.

The consumption of perfumes fluctuates with the fortunes of a nation. The early Eastern races and then the ancient Egyptians introduced perfumes into religious ceremonies, their secular use being often forbidden. Gradually, however, they became used for domestic purposes, together with many different pomades and, in some cases, dyes. Egyptian pomades were held in high

CINENE ($\Delta^{1,8(9)}$-Terpadiene or Dipentene; Inactive Limonene), $C_{10}H_{16}$, is found together with cineol in *Oleum cinæ* and also in *Laurus camphora* and in Russian and Swedish turpentine oils. It is formed by isomeric change when camphene, active limonene, pinene, etc., are subjected to protracted heating at 260° to 270°, and is obtained, together with

esteem by Cleopatra. With the ancient Greeks, the use of perfumes and cosmetics assumed considerable importance and often degenerated into abuse, and Socrates states that if even a slave is anointed with a good perfume he will exhale the same odour as his master.

Perfumery flourished under the Romans and declined with the Empire, being re-established in Italy only at the time of the Renaissance. It then passed into France, where it became a true national industry, culminating at the time of the perfumed Court of Louis XV.

Until about the middle of last century, France enjoyed almost a monopoly in this industry, but when science pervaded this branch of human activity, the French rule-of-thumb manufacturers did not grasp quickly enough the benefit to be derived from a rational development of their industry, of which England and Russia and, more especially during the past quarter of a century, Germany have taken advantage. At Grasse and Cannes, in the South of France, however, the natural perfume industry is still of importance, certain factories dealing with as much as 3000 kilos of violets (40 to 50 millions of flowers) at a time.

As has been already mentioned, the prime materials come mainly from Eastern Europe, and at the present time also from the Far East, but the cultivation of plants for perfumes is still largely carried on in the South of France and in Sicily.

In annuals the essential oil is formed in the green organs, and the majority of it is found in the flowers before fertilisation. The extraction of perfumes from flowers and leaves is carried out in various ways: (1) By *distillation* with direct or indirect steam or *in vacuo*, the distillates of different densities being separated; this method is used for *lavender, rosemary, thyme, orange blossom,* and *roses*, which are unaltered at steam heat. (2) By *infusion* for 12 to 48 hours at 60° to 65° with pure fats (olive oil, etc.), the flowers being renewed four to six times until the fat is highly perfumed; the extracted flowers are pressed to free them from fat, and the perfumed fat run into enamelled iron vessels as a concentrated pomade; in this way are treated *cassia, violets, jonquils,* and sometimes orange blossom and roses, when mixed with other flowers. (3) By *absorption in the cold* of the more delicate perfumes of *jessamine, heliotrope,* and *tuberoses:* in vessels with glass walls smeared with fat or covered with cloth soaked in oil, the petals are pressed and rubbed, being renewed every day; after some days or at the end of the season the perfumed fats are shaken for a long time with alcohol, which extracts all the perfume. To obtain colourless products, Piver passes a slow current of air through the flowers and then on to the fatty surface. (4) By *dissolution*. The use of this method is spreading, as it gives highly concentrated, very delicate perfumes. The flowers are immersed in petroleum ether, carbon disulphide, etc., the perfume being extracted by a current of steam from the solvent, which is afterwards recovered. (5) By *pressure* with hand or hydraulic presses, this method being employed with orange-peel, bergamot, iris rhizomes, etc. The yields obtained per 1000 kilos of leaves or flowers are about as follow, the prices being those of 1913: 1 kilo of *orange oil* or *neroli*, from the flowers (value £24 to £28), or 3 kilos of *petit grain* (from the leaves); 1 kilo of *essence of basil* (£6 to £8 per kilo); 1200 grms. of *essence of citronella* (88*s*. per kilo); 9 to 15 kilos of *eucalyptus oil* (from the leaves); 120 grms. of *essence of jessamine* (from fresh flowers); 1 kilo of *geranium oil* (from flowers and leaves); 10 kilos of *oil of lavender;* 6 kilos of *marjoram oil;* 2 kilos of *mint oil;* 3 kilos of *myrtle oil;* 2 to 10 kilos of *rosemary oil;* and 200 to 500 grms. of *rose oil*.

In Germany, although the climate does not seem very favourable, the cultivation of certain flowers for perfumes is largely carried on in some districts. The perfumery factories have hundreds of hectares of land under flowers, not only for commercial purposes but also for analytical and research work. One hectare yields 10,000 to 15,000 kilos of rose leaves. At one time the firm of Schimmel (Leipzig) treated as much as 600,000 kilos of fresh rose leaves per day, 300 kilos of *rose oil* being extracted; this was repeated two or three times in a month (June). A kilo of the oil is sometimes obtained from 2000 kilos of the leaves.

Rose cultivation is, however, carried on most extensively in Turkey and Bulgaria, where preference is given to the red rose (*Rosa damascæna*), which gives on an average 1 kilo of oil per 4000 kilos of leaves, although white roses (*Rosa alba*), giving 1 kilo of oil per 5000 kilos of fresh petals, are also largely grown. The product from the latter variety is less fine, but it gives an oil crystallising at 18° to 20° and is used to mask oils of lower quality; the market value of the oil is judged more particularly from the freezing-point, which should be between 17° and 19° for good qualities. Adulteration with alcohol or spermaceti is easily discovered, but it is more difficult to detect additions of geranium oil or palmarosa oil.

In 1887 Turkey produced 2400 kilos of pure rose oil (attar of roses), whilst in 1904 and 1906 the output reached 3600 kilos. The annual production varies very considerably, as the plants suffer greatly in dry seasons, especially if water is scarce in the month of May preceding the harvest; in 1907, indeed, the output was only 2000 kilos.

In Bulgaria roses are still more largely grown, and here, too, the production varies widely. At one time two-thirds of the oil went to France, but even prior to the war only one-third was sent to the French factories, one-third going to Germany, and the rest to Great Britain and the United States.

The price of *attar of roses* varied before the war from £32 to £80 per kilo, and was formerly higher than this.

In 1904 H. von Soden patented a process for obtaining more refined and delicate perfumes from flowers. He first obtained a petroleum ether extract which was then evaporated and the

isoprene, when rubber is distilled, 2 mols. of the *isoprene*, $CH_2 : CH \cdot C(CH_3) : CH_2$, undergoing condensation.

It has a pleasant odour of lemons, and boils at 176°. Nitrosodipentene (inactive carvoxime) melts at 93°. With HCl, cinene gives two stereoisomeric *dipentene dihydrochlorides* (1 : 4-dichloroterpanes), melting at 50° and 25°. The *tetrabromide* melts at 125°.

CARVENE (*d*-**Limonene, Hesperidine, Citrene**), $C_{10}H_{16}$, forms the greater part of orange-

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residue taken up in alcohol, the latter being distilled off and the residue distilled in steam. It must, however, be pointed out that with this process, 1 kilo of the finest rose oil would now cost £1520 and 1 kilo of oil of violets even more.

From what has been already stated, it will be recognised that considerable interest attaches to the study of the composition and constitution of these essences and to their artificial production by synthetical methods. In former times, various artificial perfumes have been obtained empirically, as was also the case with the first coal-tar dye, yet it has required systematic chemical investigation to open up new fields in this direction. During the last 30 years, the consumption of perfumes has increased from £480,000 to £2,400,000, owing to the diminished prices of the natural and artificial products.

The first artificial perfume was nitrobenzene or artificial myrbane oil, which was discovered by Mitscherlich in 1834, placed on the market by Colles and manufactured on a large scale by nitrating benzene from tar by Mansfield in 1847. In about 1840, Piria oxidised *salicin* (a glucoside found in willow bark) and thus obtained salicylaldehyde, which is the pleasant smelling essence of *Spiræa ulmaria* (meadow-sweet). A few years later—in 1844—Cahours succeeded in isolating the active principle of *gaultheria* or *wintergreen oil*, consisting of methyl salicylate, which can be obtained synthetically by heating salicylic acid with methyl alcohol (wood spirit) and sulphuric acid. Many of the natural perfumes contain aldehydes, and in 1853 Bertagnini showed how they could be separated pure by first combining them with bisulphite. *Benzaldehyde* was synthesised by Cahours in 1868, and *coumarin*, the essence of *Asperula odorata*, by Perkin in 1875. In 1876 Haarmann and Tiemann ascertained the constitution of *vanillin*, later preparing it from coniferin or, better still, from eugenol extracted from clove oil. In 1888 Baur prepared *artificial musk*.

In 1893 Tiemann and Krüger succeeded in effecting the synthesis of violet oil, previously obtained at enormous expense from the natural flowers. They also separated *irone*, the odorous principle of iris root, and determined its chemical constitution. Immediately afterwards they prepared synthetically an isomeride of irone, *ionone* (*see later*), to which the delicate odour of the violet is due. These investigators heated citral, which occurs in abundance in lemons, with acetone, acetic anhydride, acetic acid, and sodium acetate, obtaining first pseudo-ionone, which has an unpleasant smell, and, when treated with mineral acid, yields ionone. These processes were patented by Tiemann and disposed of by him to the most important perfume manufacturers for £40,000.

The study of the chemical constitution of the components of perfumes reveals a certain relation between the aroma and the presence of definite atomic groupings (*osmophores*) and attempts were made to establish a perfume theory on a similar basis to the colour theory of aniline dyes, the characteristic groups of which are termed *chromophores*. It has not yet been found possible to formulate a theory as rigorous as that for the colouring-matters, and all that has been fixed is that aldehydes, ketones, mixed ethers, etc., often enter into the constitution of perfumes, and that the introduction of certain alcoholic residues into the molecules may intensify or modify the aroma. The tertiary butyl group produces the odour of musk in trinitrotoluene, trinitroxylene, etc.

The action of perfumes on the olfactory nerves is not thoroughly understood, although it is regarded by some as due to vibrations of the ether similar to those by which light and heat are transmitted, these vibrations originating from the oxidation of the substance in the air. This hypothesis seems to be supported by the fact that many odorous substances emit no smell when worked and distilled in an inert gas instead of in air. It is now, however, generally assumed that the smell is propagated by small particles or molecules, which become detached and, in the state of gas, come into contact with and excite the papillæ of the nasal mucous membrane. The fact that certain substances have little smell in the pure or concentrated state and acquire their maximum smell only when considerably diluted, is well explained by modern views on solutions, dissociation in dilute solutions giving rise to the corresponding ions, which become detached and excite the olfactory sense. That minimal traces of these substances transmit perfume is shown by the retention of this property by garments which have been washed five or six times (*see* Experiment described in Vol. I., p. 4). A series of tests, controlled by the *olfactometer*, showed that most men—who have by no means a very delicate sense of smell in comparison with other animals—perceived the odour of 1 part of prussic acid in 100,000 of water, 7 per cent. of the individuals examined detecting it in a dilution of 1 in 2,000,000. Of the women tested, however, not one was able to detect prussic acid in a dilution as small as 1 in 20,000. These results support the view that male animals are very sensitive to the odour of the females, which serves to excite their sexual passions. Some individuals, termed *anosmic*, are quite without sense of smell.

The influence exercised by the artificial perfumes on the price of perfumes in general is illustrated by the fact that before the war synthetic vanillin was sold, in large amounts, at 16*s*. per kilo, whereas 30 years earlier the natural product cost up to £140. Also heliotropin cost in 1881 £100 per kilo in 1890 £15, and in 1902 not more than 30*s*.

peel oil and also occurs abundantly in cumin oil, anethum oil, etc., ; lemon oil is a mixture of pinene and limonene. It is a liquid boiling at 175° and is optically active although readily convertible into inactive dipentene. It forms a dextro-rotatory tetrabromide, melting at 104°.

l-LIMONENE, $C_{10}H_{16}$, the constitution of which is shown on p. 703 (V), can be obtained from *d*-carvone, and occurs, together with *l*-pinene, in pine oil. Its tetrabromide melts at 104°.

SYLVESTRENE, $C_{10}H_{16}$, is possibly derived from *m*-cymene and forms a dextro-rotatory component of turpentine. It boils at 176° and gives an intense blue coloration with concentrated sulphuric acid and acetic anhydride.

TERPINOLENE ($\Delta^{1,4(8)}$-Terpadiene), $C_{10}H_{16}$, has the constitution shown at IV on p. 703. It is obtained by the elimination of water from terpineol and melts at 185°.

TERPINENE, $C_{10}H_{16}$, boiling at 179° to 180°, is obtained in the transformation of various terpenes. Its nitrosite forms monoclinic crystals melting at 155°.

DIHYDROCYMENE, $C_{10}H_{16}$, obtained synthetically from ethyl succinylsuccinate, boils at 170°.

PHELLANDRENE, $C_{10}H_{16}$, is known in both the lævo- and dextro-rotatory forms, these having the same chemical and physical properties (excepting the optical rotation) and boiling at 172°. The former (*l*-) is found in Australian eucalyptus oil and the latter in *Anethum fœniculum* and in water-fennel oil (*Phellandrium aquaticum*).

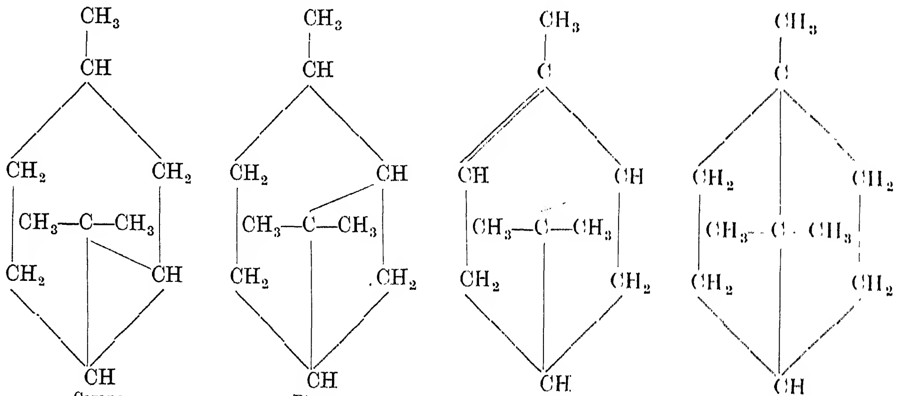
MENTHENE, $C_{10}H_{18}$, boils at 166°. MENTHANE (Hexahydrocymene), $C_{10}H_{20}$, boiling at 170°, does not occur naturally, but is obtained by hydrogenating cymene in presence of nickel.

COMPLEX TERPENES

Like the preceding, these are composed of a monocyclic system, but with two rings ; they have only one double linking, and hence combine with two atoms of hydrogen or halogen.

They can be converted readily into cymene and its derivatives.

The following four diagrams show how a trimethylene ring or *bridge* is formed in Carane (not known in the free state, although the corresponding saturated, synthetic ketone, Carone, is known), a tetramethylene ring in pinane and pinene, and a pentamethylene ring in camphane :



Carane Pinane Pinene Camphane

PINENE (Terebenthene, Laurene, Menthene, etc.), $C_{10}H_{16}$ (constitution, *see above*), forms one of the principal components of oil of turpentine, occurs also in sage and juniper oil, and, mixed with sylvestrene and dipentene, forms Russian and Swedish turpentine oil.

When incisions are made at suitable seasons in certain varieties of pine, fir, and larch, a kind of balsam is exuded in the form of a juice which gradually changes to a soft resin, more or less clear according to the quality. This is known as *ordinary turpentine* or American, French, Venetian, according to the particular tree and to the locality of origin.

Ordinary turpentine consists mainly of resin acids (abietic and other acids and the corresponding products of acid oxidation), its saponification number being 155 to 195 and its iodine number about 150. When turpentine is distilled with steam, the liquid *essence*

or *oil of turpentine* (turps) is collected separately, the residue, which is solid in the cold, being **Colophony.**[1] The direct extraction of the turpentine from resinous woods or tree stumps by means of suitable solvents has been suggested. The stumps are first cleaved by explosives and then sawn up and rasped, the fine mass being distilled with steam to recover turpentine oil and the residue extracted with benzene or trichloroethylene or hot wood tar mixed with pine oil (U.S. Pat. 852,236); after recovery of the solvent by distillation, a dense mass remains composed of 90 per cent. of colophony and 10 per cent. of oil of turpentine. Oil of turpentine is rectified by heating with steam in presence of 0·5 per cent. of quicklime. As the oil always resinifies to some extent when exposed to the air, it is often desirable to redistil it before use. The strong and less agreeable odour of Russian and Greek turpentine oils is removed or lessened by shaking with a solution of permanganate, dichromate, or persulphate.

Fresh oil of turpentine is clear, colourless, and highly mobile; it has the sp. gr. 0·855 to 0·876 and boils at 156° to 161°. It absorbs and combines with considerable quantities of ozone and oxygen—part of the latter being converted into ozone and the oil at the same time resinifying. It dissolves sulphur, phosphorus, rubber, and resins, and is hence used for varnishes, lacs, oil paints, etc.[2]

Permanganate in acid solution transforms it partly into **Pinonic acid**, $C_{10}H_{16}O_3$, while with dilute nitric acid it gives **Terephthalic** and **Terebinic acids**, $C_7H_{10}O_4$. It reacts violently with iodine in the hot, forming cymene. The relation between resins and aromatic compounds is established by the fact that when the former are distilled with zinc dust they form aromatic hydrocarbons, while if fused with potash they give di- and tri-hydroxybenzenes. Resin substitutes or *artificial resins* are now prepared by heating phenols with formaldehyde (*see* Baekelite, p. 641).

According to the preponderance of lævo- or dextro-pinene, turpentine oil is lævo-rotatory (Venetian, German, and French) or dextro-rotatory (Australian).

Pinene contains only one double linking, and hence unites with only 1 mol. of HCl, giving **Pinene hydrochloride**, $C_{10}H_{17}Cl$, which melts at 125°, and has the smell of camphor (**artificial camphor**). When treated with alcoholic potash, this hydrochloride is converted

[1] **COLOPHONY** (*rosin*) is hard and brittle, its sp. gr. being 1·050 to 1·085 at 15° and its fracture shining and conchoidal. According to the quality, its colour varies from yellow to brown, but it gives a whitish powder. At 70° it becomes soft and it forms a kind of emulsion with hot water. It always melts below 135° and it is readily soluble in alcohol (1 in 10), ether, benzene, petroleum ether, and carbon disulphide. It burns with a smoky flame and, when subjected to dry distillation out of contact with the air, yields *resin oil*. It contains *abietic acid*, $C_{19}H_{28}O_2$, which has two double linkings, melts at 165°, and is soluble in hot alcohol. From *gallipot rosin* (*Pinus maritima*) *pimaric acid*, $C_{20}H_{30}O_2$, m.-pt. 148°, has been obtained.

Colophony has the rotatory power − 69·6°, and the acid number 145 to 185.

One cu. metre of fir contains about 10 kilos of turpentine, which yields as much as 7 kilos of colophony, while 1 cu. metre of pine gives 22 kilos of turpentine, this leaving 16·6 kilos of colophony; the larch gives an intermediate yield.

Colophony is used in large quantities for mixing with soaps (*see* Resin Soaps, p. 518), for sizing paper, for making varnishes, mastics, etc. In the United States 35 per cent. of the total output is used in soap-making.

Large quantities of it are incorporated with artificial wax (cerasin), which is thus cheapened; to *deodorise* the resin, it is finely ground, macerated with dilute sulphuric acid for 5 or 6 days and then suspended in hot water and subjected to a jet of steam for some time. After this treatment it melts and mixes well with the cerasin.

Colophony is also used for making sealing-wax by mixing with shellac, turpentine, and a larger or smaller number of mineral substances (chalk, burnt gypsum, magnesia, zinc oxide, baryta, kaolin, etc.), according to the quality required; the fused mass is coloured with cinnabar (for the finer red qualities), minium, ferric oxide, or red ochre. The best qualities contain only 40 per cent. of mineral matter and are mainly shellac, while the inferior kinds contain as much as 70 per cent. of mineral matter, the residue being principally colophony. Sealing-wax is coloured black by lampblack or boneblack, green by Prussian blue, yellow by chrome yellow, or blue by ultramarine; when fused, colophony may be coloured also with algol or indanthrene dyes (*q.v.*). Substitutes for sealing-wax are now prepared from artificial resins (*see* p. 641).

Copal resin has already been described (p. 495). *Dammar*, a similar resin, gives fine, pale varnishes; Australian dammar or copal is known also as kauri gum.

[2] **Oil of Turpentine** consists almost entirely of *l*-pinene (*terebenthene*) and *d*-pinene (*australene*). The most common commercial varieties are French, English, Russian, German and American.

The smell of European turpentine oil has been improved by treatment with oxidising agents, such as permanganate, persulphates, or chromic acid, or, better still, with hydrogen peroxide, sodium peroxide, barium peroxide, or oxides of nitrogen.

By suitable application of Halphen's reagent (p. 637) or mercuric acetate, C. Grimaldi (1910) was able to detect adulteration with pine oil or resin oil.

into CAMPHENE, $C_{10}H_{16}$, m.-pt. 50°, which is known in three optical modifications and is transformed by oxidising agents into camphor and by ozone into the ozonide (Harries, 1910), these reactions establishing its constitution. FENCHENE is similar to camphene but is an optically inactive liquid, boiling at 158° to 160°; it resists the action of nitric acid, but not that of permanganate.

CAMPHANE, $C_{10}H_{18}$, forms white volatile crystals melting at 154° and boiling at 160°, and is obtained by reducing *d*- or *l*-bornyl iodide. It is optically inactive, and is the saturated hydrocarbon of the camphor nucleus.

HOMOLOGUES OF TERPENES. The most interesting lower homologue is Hemiterpene or Isoprene, C_5H_8 (*see* p. 109), which gives various terpenic polymerisation products, such as $(C_5H_8)_3$ (Clovene, Cedrene, Caryophyllene, etc.), $C_{20}H_{32}$ (Colophene), $C_{10}H_{16}$ (Rubber), etc.

RUBBER (*caoutchouc*) is obtained from the milky juice (*latex*) exuding when incisions are made in the stems of certain plants growing in the tropical regions of South America (especially Brazil), East and West Africa, Asia and Polynesia (Ceylon, Malacca, Sumatra, Java, etc.). The plant families giving rubber are: *Euphorbiaceæ* (the genus *Hevea brasiliensis* of Brazil and Ceylon gives the best *Para* rubber; *Manihot*, also of Brazil, etc.); *Moraceæ* (especially the *Ficus elastica* of the East Indies and the *Castilloa* of South America); *Apocyneæ* (especially the genus *Laudolphia*, growing in Africa), etc.

FIG. 463.

In some districts the trees were formerly cut down to obtain the rubber, but nowadays V-shaped or spiral or herring-bone incisions are skilfully made in the bark (Fig. 463), the latex being collected each day. When the growing use of the automobile involved a great increase in the demand for rubber, plantations were laid out with selected seeds and plants, which are carefully cultivated.

Coagulation of the Rubber is an important and delicate operation. According to Henri (1906–1908), the faintly alkaline latex contains the rubber, ready formed, in the form of minute emulsified drops (50 millions per c.c.), which are in continual movement, and of which this author was able to obtain a cinematographic representation; a coagulum is produced by acids, by salts of divalent metals (Ca, Mg, Ba, etc.), and less rapidly by salts of trivalent metals, etc., but not by alkalis. The conditions of coagulation, which are not identical with different varieties of latex, are in general related to the quality of the rubber yielded. The best quality (*Para rubber*) is obtained by drying superposed thin layers of fresh latex in a mould by means of hot gases until about a hundred layers, each about 0·5 mm. in thickness, are obtained. The commoner qualities are set by the heat of the sun, with addition of acid and water; the electrolytic separation of rubber has also been suggested (Ger. Pat. 218,927, 1908), but better results appear to be obtained with HF or CO_2 (Pahl, Ger. Pat. 237,789, 1910) or with formalin or a trace of mercuric chloride. Various plant juices, salt solutions, soap solution, etc., are also used.

The ideal coagulant should leave the proteins unchanged and should form harmless salts with the mineral constituents. Such substances as acetic acid do not answer these requirements. The coagulating action of smoke, used by the natives, is due to the carbon dioxide present, this being, unlike other coagulants, harmless in excess. Frank and Marckwald (1912) obtain good results with tannin. Coagulation by heating in churns or by centrifugation is spreading nowadays. To preserve the latex and prevent oxidation, the addition of 4 grms. of hydrosulphite per litre has been suggested.

The coagulated rubber is marketed in different forms [1] and is distinguished as: American (Brazil, Mexico), African (tropical, East and West Africa), and Asiatic (Malay States, Polynesia, etc.). All these forms are brown or almost black outside but pale brown or almost white inside.

Raw Rubber has sp. gr. 0·91 to 0·97 and is of more or less unpleasant odour. It is highly elastic at ordinary temperatures but only slightly so at 0°. When pasted for some time at 60° it becomes plastic and loses its elasticity, which is regained at ordinary temperatures.

[1] Rubber is sold as *crêpe*, balls (10 to 50 kilos) and marbles (3 to 5 kilos), sheets, laces, flats, buttons, cakes or biscuits, scraps or niggers, strips, twists, clusters, thimbles, flakes and lumps.

At 100° it becomes soft, and at 140° viscous, and at 180° it melts, the original properties being regained only slowly at ordinary temperature. It is a good electrical insulator, is insoluble in cold water, and swells in hot water or alcohol; it swells even more and dissolves slightly in carbon bisulphide, benzine, ether or oil of turpentine, and completely in rubber oil obtained by the dry distillation of rubber. It resists the action of alkalies and dilute acids, but in the air oxidises slowly at the surface, undergoing resinification and becoming friable. When heated it dissolves considerable amounts of sulphur, assuming new properties which render possible its application for many purposes (*see later*, Vulcanisation).

Treatment of Rubber. The raw product is softened in hot water and then repeatedly subjected to great pressure between iron rollers revolving at different rates, impurities being washed away by means of a water spray. The loss attending this treatment amounts to 10 to 40 per cent.

The product is then *masticated* to give a homogeneous mass free from pores. Strips are placed in a stationary, horizontal drum inside which a second drum, furnished with teeth or veins, and heated internally, revolves eccentrically. During this treatment and the succeeding passage of the rubber between two tepid cylinders rotating at different rates, the various mineral filling materials for colouring or weighting (10 to 50 per cent.) the rubber may be introduced, together with the necessary amount of sulphur (4 to 15 per cent.) for the subsequent vulcanisation. For colouring use is made of antimony or mercury cinnabar, ferric oxide, or ochre, barium sulphate, zinc white, lithopone, gypsum, talc, chalk, kaolin, magnesia, etc., being employed as *fillers*.[1] Other additions are also made for obtaining the various qualities of rubber required for making different articles.

Rubber thus prepared is then *vulcanised*, the strength and elasticity being thus enhanced, and the rubber rendered more stable towards changes of temperature and to oxidation. Vulcanised rubber is not soluble at ordinary temperatures in the usual solvents of raw rubber, is not tacky in the cold, is almost impervious to water, and more resistant towards acids, alkalies and the air, and maintains its elasticity between − 20° and + 120°. Dichloroethylene (dieline, *see* p. 122) forms a good solvent for it.

Vulcanisation with sulphur was suggested in 1839 by Goodyear and by Hancock, the rubber being mixed with sulphur and heated at 120° to 140°. Addition of various substances (oxides of lead, zinc, magnesium, calcium, etc.) in small amounts as *accelerators of vulcanisation* has been proposed, and nowadays the time required is considerably shortened by means of *organic accelerators*, *e.g.*, piperidine, aldehyde-ammonias, *p*-phenylenediamine, the nitroso-derivatives of dimethylaniline, diphenylamine, methylaniline, etc., or, better, the dithio-derivatives of imino-bases, *e.g.*, dimethylammonium dimethyldithiocarbamate and piperidine piperidyldithiocarbamate (Bayer, 1915).

A system of rapid vulcanisation, long known and widespread at the present time, is the so-called *cold vulcanisation*.[2]

[1] Addition of 0·5 per cent. of zinc oxide to rubber increases by 0·26 per cent. the sulphur combined during vulcanisation and also increases the tenacity and resistance to torsion, further addition being without effect. Magnesia behaves almost like zinc oxide, but talc is indifferent or harmful.

[2] **Rapid cold vulcanisation**, proposed by Parkes in 1846, consists in immersing the rubber in a solution of sulphur chloride in carbon disulphide. Henriques (1893) showed that the sulphur chloride combines with the rubber, this result being confirmed by Weber (1894). Later, Hinrichsen, Kindscher and Bernstein found that 2 mols. of rubber unite with 1 mol. of the chloride, giving the compound $(C_{10}H_{16})_2$, S_2Cl_2 (15 per cent. of S), the addition taking place in the same way as that of sulphur chloride to ethylene, amylene, etc. Since, however, a rubber containing 5 per cent. of sulphur is over-vulcanised, that is, hard and brittle, the chemical interpretation of the phenomenon is insufficient.

E. Stern (1909) holds that the quantity of sulphur fixed is variable, while Ostwald (1910) explains vulcanisation as an *adsorption* phenomenon of the colloidal rubber, and assumes that the sulphur forms a series of reaction products, the first and last members of which cannot be isolated, and that the process is partly reversible. Other explanations have been advanced by Spence and Young (1912), Skellon (1913), Bisow, Bruni and Amadori (1919), etc.

In practice, use is made of 2 to 4 per cent. solutions of sulphur chloride in carbon disulphide or benzine, which is safer. The rubber articles are immersed in the solution for a few seconds or minutes, according to the thickness of the material and the degree of vulcanisation required. Small and thin objects may be readily vulcanised in the vapour of sulphur chloride, rendered more volatile with a little carbon tetrachloride. Peachey (Eng. Pat. 129,826, 1919) obtains rapid and complete vulcanisation in the cold by producing nascent sulphur within the rubber by alternate treatments with hydrogen sulphide and sulphur dioxide.

In general, the sulphur chloride process gives a too superficial vulcanisation. Bruni's process (1920), which appears more satisfactory, consists in forming in the rubber thiocarbanilides or

With age, rubber (tubing, etc.) becomes hard and brittle, and cracks. According to Wo. Ostwald (Ger. Pat. 221,310 of 1908), it lasts longer if quinoline, aniline, dimethylaniline, etc., is used in its preparation. Introduction of excess of sulphur during vulcanisation causes rubber to deteriorate more easily in the air; in some cases the excess of sulphur is eliminated by treatment with hot soda solution. Small articles keep well in closed vessels containing petroleum.

In the regeneration of rubber from old vulcanised articles, the material is freed as far as possible from vegetable and mineral impurities and from any portions containing textile fabric. The necessary removal of the sulphur cannot be effected by solvents, which dissolve only the free sulphur. The sulphur compound of rubber consists of a more or less highly condensed product of $C_{10}H_{16}$ with $C_{10}H_{16}S_2$ (or S_2Cl_2), and many processes have been devised for the removal of the sulphur from this complex. Rubber rich in combined sulphur, *i.e.*, hard rubber (ebonite) is not readily devulcanised and is usually powdered and used in making fresh ebonite. If not too hard, rubber free from fabric is disintegrated and impregnated while hot with fatty or mineral oils, paraffin wax, etc., the resulting product being mixed and passed between hot rollers so as to obtain elastic sheets.

Waste containing fabric (goloshes, tyres, etc.) is occasionally treated mechanically, being powdered and then winnowed to eliminate the particles of fabric. Such separation is, however, imperfect and it is preferable to dissolve out the rubber rather than the fibres by means of solvents. The Mitchell process consists in dissolving the fibre in hot 65 to 70 per cent. sulphuric acid, the mass being washed with water and dilute caustic soda and then rendered plastic by steam and hot rollers; this procedure does not, however, remove mineral constituents (chalk, zinc oxide, etc.). The alkaline process suggested by Marks (1899) gives better results, and consists in heating the waste rubber with 10 per cent. caustic soda under pressure, the hydrocellulose being removed and the residual rubber well washed and rolled hot; the caustic soda dissolves also fatty oils (*i.e.*, of *factis*).

In the processes of the other class, the rubber is dissolved in hot benzene or its homologues or certain chloro-compounds (dieline), the extraction being carried out in ordinary extractors or in autoclaves.

According to Hinrichsen and Kindscher (1912) cold vulcanised rubber may be completely desulphurised by heating it for several days in a reflux apparatus with alcoholic caustic soda and scrap copper, and hot vulcanised rubber by heating, in a copper-lined autoclave, with benzene, caustic soda and zinc. Various other methods have also been suggested. Sachs (Ger. Pat. 275,061, 1913) utilises old powdered rubber by mixing it with 20 per cent. of colza oil and 50 per cent. of magnesium sulphite and heating at a pressure of 5 to 7 atmos. for 20 to 30 hours.

Regenerated rubber contains at most 80 per cent. of true rubber and sometimes only 25 to 30 per cent., but is little inferior to virgin rubber. The *coefficient of vulcanisation*, that is, the amount of combined sulphur per 100 parts of rubber, does not exceed 4 to 5 in recovered rubber.

USES OF RUBBER. Rubber is used in enormous quantities in making tyres, waterproof fabrics, horse shoes, gloves, hosepipes, floor coverings, artificial leather and sponges, toys, etc. Mixed with guttapercha [1] and sawdust it is used to make *kamptulicon*, and large amounts are utilised in the manufacture of ebonite.[2]

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other disubstituted aromatic thioureas, *e.g.*, $2C_6H_5 \cdot NH_2 + CS_2 = H_2S + CS(NH \cdot C_6H_5)_2$, the action being accelerated by sulphur or zinc oxide.

Romani (1920) finds that tetra-alkylthiouram disulphides, *e.g.*, $((CH_3)_2N \cdot CS \cdot S \cdot S \cdot CS \cdot N(CH_3)_2$, form ultra-auto-accelerators, as they vulcanise in 15 minutes at 145° in presence of zinc oxide, addition of free sulphur being unnecessary.

Scott and Bedford (1920), who obtained the same results as Bruni (*see above*) by using piperidine in place of aniline, attribute the accelerating action to the formation of zinc piperidyldithiocarbamate.

[1] **GUTTAPERCHA** resembles rubber, but is more resinous and is obtained from the latex of various plants of the Sapotaceæ family growing in Singapore, Malacca, Borneo, Sumatra, Java, Banca, etc. It occurs to the extent of 10 to 12 per cent. also in the trunk, branches and leaves and may be extracted by means of solvents such as toluene, petroleum ether, carbon disulphide. Its specific gravity is about 0·97 or, when rolled, up to 1·02. Between 45° and 60° it is highly plastic and may be drawn into thin threads and welds readily with itself. It melts at about 120° and at higher temperatures decomposes, giving a repulsive odour. It is a bad conductor of heat and electricity, and becomes electrified when rubbed. It dissolves in benzene, chloroform, oil of turpentine, etc., and to a slight extent in alcohol, ether and petroleum ether, but is insoluble in water. It resists the action of dilute acids.

Guttapercha contains 76 to 84 per cent. of *gutta* (a solid hydrocarbon, m.-pt. 53°), 14 to 15 per

[2] For this note *see* next page.

SYNTHETIC or ARTIFICIAL RUBBER must not be confused with rubber substitutes.[1] During the European War large plant was erected at the works of Fr. Bayer at Leverkusen for the production of 2000 tons of synthetic *methyl rubber* per annum. When the war ceased the manufacture was abandoned owing to the enormous increase in the production of natural rubber and to the low prices prevailing.

The *chemical constitution* of the hydrocarbon of rubber, $C_{10}H_{16}$, was determined by Harries (1905) by means of its *ozonide*, $C_{10}H_{16}O_6$, which decomposes into levulinic aldehyde, so that the hydrocarbon must be regarded as derived from an 8-carbon atom ring (a ring never yet found in natural products);

$$\begin{array}{l} CH_3 \cdot C \cdot CH_2 \cdot CH_2 \cdot CH \\ \;\;\;\;\;\;\;\;\; \| \; \| \\ \;\;\;\;\;\; CH \cdot CH_2 \cdot CH_2 \cdot C \cdot CH_3 \end{array}$$

(dimethylcyclooctadiene). The results of later work (1907–1914) led Harries to abandon this formula, since decomposition of the ozonide of α-iso-rubber (obtained by heating the hydrochloride of rubber with pyridine under pressure) yields, besides levulinic aldehyde, also marked quantities of diacetylpropane, undecatrione, pentadecatetrone, formic, levulinic and hydrochelidonic acids, etc. These products, especially the pentadecatetrone, $CH_3 \cdot CO \cdot [CH_2]_3 \cdot CO \cdot [CH_2]_3 \cdot CO \cdot [CH_2]_3 \cdot CO \cdot CH_3$, exclude the view that the nucleus of rubber is formed from an 8-carbon atom ring, rings of 12 or 16 atoms being ruled out for other reasons. Most probably rubber contains a ring of 20 carbon atoms, which may yield numerous isomerides:

$$CH_2\left\langle\begin{array}{l} CH_2 \cdot \overset{CH_3}{\dot{C}} : CH \cdot CH_2 \cdot \overset{CH_3}{\dot{C}} : CH \cdot CH_2 \cdot CH \\ CH : \underset{CH_3}{\dot{C}} \cdot CH_2 \cdot CH_2 \cdot CH : \underset{CH_3}{\dot{C}} \cdot CH_2 \cdot CH_2 \cdot CH \end{array}\right\rangle C \cdot CH_3$$

The molecular weight of the corresponding penta-ozonide in benzene (in place of acetic acid, formerly used) is 535, approximating to the formula $C_{25}H_{40}O_{15}$, so that isoprene rubber would be a pentamethylcycloeicosanediene. Butadiene rubber will not contain the five methyl groups, whereas dimethylbutadiene rubber will contain ten methyl groups, numerous isomerides being possible in both cases.

In 1909 Harries and Hoffmann obtained an artificial rubber by polymerising isoprene in presence of glacial acetic acid in sealed tubes at 100°: $(2C_5H_8)_x = (C_{10}H_{16})_x$, but the process is too expensive to be used industrially. The firm of Bayer (Elberfeld) also obtained

[1] **RUBBER SUBSTITUTES.** Many of these have been prepared, but the only one of much practical importance is the so-called *factis*, of which two types are on the market: white and brown or black. The latter is made by boiling rape oil or linseed oil in an open vessel for two hours, cooling, and passing a current of air through it for 36 hours. It is then vulcanised by adding 2 per cent. of flowers of sulphur, heating for two hours at 140°, adding a further 1 per cent. of sulphur, and raising the temperature to 150°, when it begins to rise. White factis is obtained by treating the oil with 20 to 25 per cent. of sulphur chloride (free from dichloride); the energy of the reaction may be modified by adding the sulphur chloride dissolved in carbon disulphide. The mass is obtained in sheets or blocks by pouring it immediately on to cold metal plates or moulds. These substitutes are almost as elastic as rubber and are used to adulterate rubber; they are insoluble in water or acid, but dissolve slightly in dilute alkali. They are distinguished from rubber by being saponifiable with alcoholic potash.

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cent. of *albanan* (white, crystalline substance, m.-pt. 195°, soluble in hot alcohol, in benzene, etc.) and 6 to 4 per cent. of *fluavil* (yellowish resin, m.-pt. 110°, soluble in cold alcohol).

It is used as an electrical insulator, for making tubing and vessels resistant to alkalis and dilute acids, for making mastics and varnishes, and also in electroplating, as it takes the finest impressions. It yields vulcanised products like rubber and hard materials like ebonite. It costs rather less than rubber.

BALATA, similar to guttapercha, is obtained from the latex of *Mimusops balata* (Sapotaceæ), a large tree of Venezuela, Brazil and, especially, British and Dutch Guiana. It is used as an insulating material and for making waterproof shoes and power transmission belts. Its price is about one-half that of rubber.

[2] **EBONITE** is obtained by mixing rubber with 30 to 40 per cent. of sulphur and with various mineral substances (zinc sulphide, chalk, lead carbonate, heavy spar, magnesia, pigments, etc.), compressing the material in moulds, coating the objects with tinfoil and vulcanising at 130° to 150° for some days.

It is a hard brown or black material, which is a poor electrical conductor, expands considerably when heated, and is resistant towards alkalis and dilute acids. Under pressure the various solvents dissolve first the sulphur and then the rubber, the mineral matter remaining. It may be turned in the lathe and polishes well, and becomes plastic when warmed. It is used for making many varied articles (boxes, combs, buttons, accumulator boxes, gramophone discs, knife handles, batons, etc.; mixed with emery it is used for artificial grindstones).

artificial rubber from isoprene and from erythrene C_4H_6 (*see* p. 109 ; *also* Ger. Pat. 235,423 and 235,686 of 1909 and Fr. Pat. 425,582 of 1911), by prolonged heating in presence of benzene, etc., but this product is also very expensive.

The Badische Anilin- und Soda-Fabrik (Ludwigshafen) obtained rubber by heating isoprene and dimethylbutadiene (Fr. Pats. 417,170 and 417,768 and Eng. Pat. 14,281 of 1910) in presence of alkali, which has a polymerising action. Contrary to Weber's statement, Hinrichsen (1909) showed that the latex of rubber trees does not contain diterpenes, which polymerise to form rubber, but that the latter exists ready formed in the latex.

Synthetic rubber obtained from the isoprene formed on decomposition of turpentine, cannot be vulcanised (unless a little natural rubber is added), whereas that obtained from the isoprene of rubber is vulcanised with less difficulty.

The polymerising action of sodium on isoprene which yields rubber even in the cold, was discovered by Matthews in 1910 and by Harries shortly afterwards.[1]

STATISTICS AND PRICES. In 1840 the world's consumption of rubber was only 400 tons, but after 1860, when methods of vulcanisation had been studied, the consumption began to increase enormously.

The World's output of rubber (in tons) from the old forests and the new plantations was as follows :

	1905	1910	1913	1915	1916	1917	1918	1919	1920	1921
Brazil . .	35,000	40,800	39,370	37,220	34,500	37,000	25,000	35,500	30,000	20,000
Africa, Mexico, etc.	27,000	21,000	21,000	13,600	—	16,528	10,629	11,135	9,915	3,000
New Plantations.	145	8,200	47,618	107,867	—	213,070	255,950	285,225	308,816	270,000
Total . .	62,145	70,000	107,988	158,687	—	265,698	291,579	331,860	348.731	293,000

[1] **ISOPRENE** is obtained in 25 per cent. yield by heating oil of turpentine, as proposed by Tilden. By working under reduced pressure and first preparing dipentene, Staudinger and Gottlob raised the yield to 65 per cent., but even then the supply of oil of turpentine is inadequate and its price too high. On this account the firm of Fr. Bayer prepared isoprene by treating acetone and its homologues with formaldehyde and dimethylamine so as to obtain methylamine oxides which, by the further action of methyl halides and subsequent decomposition of the resulting ammonium compounds, lead to isoprene.

The Badische Anilin- und Soda-Fabrik obtained isoprene by converting amyl alcohol into trimethylethylene, chlorinating in a vacuum, and removing 2HCl catalytically ; this process depends on a supply of amyl alcohol, which is formed in small amount during alcoholic fermentation. Trimethylethylene was then obtained quantitatively from the pentane, isopentane and tetramethylmethane occurring in petroleum.

Polymerisation of isoprene, by either heat or sodium, yields an abnormal rubber which vulcanises incompletely and has, as fundamental constituent, a hydrocarbon different from that of natural rubber, and is partially soluble in benzene. The Badische Company obtained from isoprene normal rubber, which is insoluble in or only slightly swollen by benzene and exhibits great tenacity, by two different methods : (1) by treating isoprene with the ozonide of terpenes or other unsaturated compounds, a good yield of so-called *ozone rubber* is obtained ; (2) by condensing with sodium in presence of CO_2, *carbon dioxide rubber* being thus formed. The differences between the various artificial rubbers probably depend on differences in the degree of polymerisation. Of interest also are the methods of obtaining isoprene by pyrogenic decomposition of crude petroleum and its residues, although all the petroleum in the world would not yield more than 10 per cent. of the rubber derived from plantations.

The preparation of *s*-dimethylbutadiene, $CH_2 : C(CH_3) \cdot C(CH_3) : CH_2$—by converting acetylene successively into acetaldehyde, acetic acid and acetone, this by reduction (with aluminium and acetic acid) giving pinacone and the latter, by dehydration, dimethylbutadiene—polymerisation of which yields *methyl rubber*, is not economically practicable nowadays. The same is the case with the preparation of isoprene from isopentane (2-methylbutane) by the following stages : chloroisopentane (with Cl) $\longrightarrow$ trimethylethylene (amylene or pental), $C(CH_3)_2 : CH \cdot CH_3$ (by red-hot lime) $\longrightarrow$ dichloroisopentane (with Cl), which, if passed as vapour over alumina at 400°, gives isoprene or isomerides which yield isoprene when heated with catalysts.

The practical difficulties encountered in the Bayer works at Leverkusen were very great, and only at the beginning of 1918 was a methyl rubber K (polymerised in the cold) obtained which yielded a good ebonite and a methyl rubber W (polymerised hot), which resembled natural rubber somewhat also in its behaviour towards solvents, and served for making tyres and rubbered fabrics. The polymerisation occupied, however, as much as three months ; the vulcanisation was completed by means of various accelerators (*see* above), such as piperidine or, better, *p*-phenylenediamine, *p*-aminoazobenzene, toluidine, etc., which also protect the rubber against atmospheric oxidation. Substances capable of increasing the elasticity of these synthetic rubbers may also be added.

The consumption in tons in different countries in 1920 (1919) was: United States, 220,000 (230,000); Great Britain, 25,000 (33,000); France, 14,000 (22,000); Italy, 6000 (14,000); Canada, 11,000 (9500); Australia and Japan, 9000 (10,000); Germany, Russia and Austria, 9000 (5500); Scandinavia, 6000 (3500); Belgium, 2000 (2000); various other countries, 1000 (3500).

Experts calculate that the total output of rubber will be about 420,000 tons in 1922, 470,000 in 1923, 520,000 in 1924, and almost 600,000 tons in 1925, in spite of restrictions imposed by an association of the principal producers.

The price of rubber has fallen greatly in recent years, owing to increased output and diminished demand, and in 1921 was less than 1*s.* and in March, 1922, 8*d.* per lb.

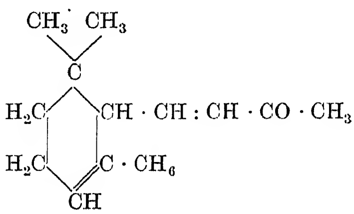
OXYTERPENES

Other hydrocarbons related to the terpenes are: *ionene* and *irene*, two isomerides of the formula, $C_{13}H_{18}$, the ketones of which, $C_{13}H_{20}O$, are *irone* and *ionone*, *i.e.*, the aromatic principle of iris root, having a marked violet smell.

IONONE (Artificial essence of violets) was prepared synthetically by Tiemann and Krüger in 1883 by shaking equal proportions of citral and acetone with barium hydroxide solution, extracting with ether and expelling the latter by evaporation.

The fraction of the residue boiling at 138° to 155° is pseudoionone, which is transformed into the isomeric ionone by the action of dilute acid (Ger. Pat. 75,120). According to Ger. Pat. 113,672, the condensation may be effected by water in an autoclave at 170°, while in presence of sodamide it takes place at the ordinary temperature (Ger. Pat. 147,839). *See also* Ger. Pat. 138,939.

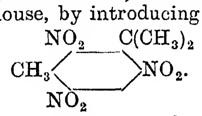
The constitution of synthetic ionone is represented by the annexed formula:



Ionone (100 per cent.) cost before the war £152 per kilo, and *β-ionone*, £60; the 20 per cent. solutions were sold at one-fifth of these prices.

MUSCONE, $C_{15}H_{28}O$ or $C_{16}H_{30}O$, is the odoriferous component of *natural musk*, which is obtained from a pouch situated behind the navel of the male musk-deer (*Moschus moschiferus*), living in the mountains of Central Asia (Thibet, Tartary, Siberia, Cochin China, Tonkin, China). The entire pouches are placed on the market and weigh 20 to 40 grms., 60 per cent. consisting of musk. Of the latter, 60 to 70 per cent. dissolves in water (and effervesces with acids), 10 to 12 per cent. in alcohol, and very little in ether, chloroform or benzene; the moisture amounts to 15 per cent. and the ash to 8 per cent. Musk contains fats, albuminoids, ammonium carbonate and 0·5 to 2 per cent. of a volatile oil which distils in steam and forms *muscone* (density 0·9268, rotation + 10°, b.-pt. 330°), which is a ketone and has a very intense, pure odour of musk. Before the war, Tonkin musk in the pouch was sold at about £140 per kilo and Siberian at less than £80. Musk is often largely adulterated. The price fell as a result of the manufacture of *artificial musk*.[1]

[1] **ARTIFICIAL MUSK** has not the composition of muscone, but has the same marked odour, although a little less delicate. It was prepared by Baur in 1888, and manufactured by the Fabriques de Produits Chimiques de Thann et de Mulhouse, by introducing into *s*-trinitrotoluene the tert.-butyl group, the constitution being:



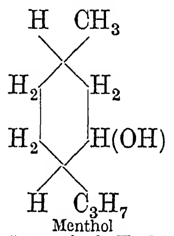
Of the many chemically analogous products very few have the musk odour, among these being xylol musk, obtained by condensing *m*-xylene with tert. isobutyl chloride in presence of aluminium chloride and nitrating the pseudobutyl-*m*-xylol thus formed. The purified product has m.-pt. 113° and, diluted with nine times its weight of acetanilide to attenuate the excessively powerful perfume, was at first sold at £100 per kilo, natural musk then costing £200 per kilo. Various similar products have been made.

CAMPHORS

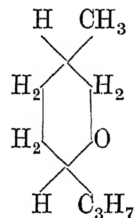
While the terpenes are liquids, the camphors are generally solid. They contain alcoholic or ketonic oxygen and the principal ones with a single ring are: **Methone**, $C_{10}H_{18}O$, and **Terpinol** with the same formula, while **Menthol** and **Carvomenthol** are $C_{10}H_{20}O$, and **Terpin** $C_{10}H_{20}O_2$. Among the camphors with complex rings are true **Camphor**, **Fenchone**, and **Carone**, $C_{10}H_{16}O$, and **Borneol**, $C_{10}H_{18}O$.

The camphors poorer in hydrogen and oxygen contain double linkings, form additive products, and are readily oxidised, while the others behave like saturated compounds.

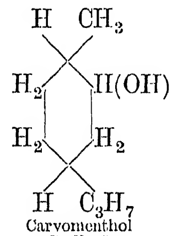
When reduced with sodium, the ketonic camphors yield the alcoholic camphors, which are converted into the former on oxidation. It is possible to pass from the camphors to the terpenes by way of the chlorides, and reduction of the alcoholic camphors often gives the terpene hydrocarbons. Thus, **Terpane** (*hexahydrocymene*) can be obtained by reducing the **Terpanol** (*menthol*, $C_{10}H_{20}O$), which contains a hydroxyl or secondary alcoholic group, this being transformed by oxidation into the ketonic group with formation of **Terpanone** (*menthone*),[1] so that the hydroxyl should be in the ortho-position with respect to the CH_3 and C_3H_7 groups, as is shown below in the constitutional formulæ. On the other hand, since **Carvacrol**, $C_6H_3(\overset{2}{OH})(\overset{1}{CH_3})(\overset{4}{C_3H_7})$ (isomeric with carvone or carvol) of known constitution, gives on reduction a terpanol (*carvomenthol*, with the hydroxyl in the position 2) different from that of menthol, the hydroxyl of the latter must be in position 3:



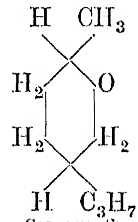
Menthol (terpanol), $C_{10}H_{20}O$



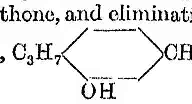
Menthone (terpanone), $C_{10}H_{18}O$



Carvomenthol $C_{10}H_{20}O$



Carvomenthone $C_{10}H_{18}O$

MENTHOL (3-Terpanol), $C_{10}H_{19} \cdot OH$, occurs in abundance in oil of peppermint, from which it can be obtained crystalline by cooling. It melts at 42°, boils at 213°, and has the strong odour of peppermint. The position of the OH is established by the fact that, with bromine in chloroform solution, *menthone* (which is the corresponding ketone, boiling at 207°, and also having a strong smell of peppermint) gives dibromomenthone, and elimination of 2HBr from the latter gives thymol having the known constitution,  ; the CH_3 and OH are here undoubtedly in the meta-position, since elimination of the C_3H_7 by means of P_2O_5 yields *m*-cresol. When heated with copper sulphate, menthol yields cymene. Four isomerides of menthol are possible theoretically. It is used as an anæsthetic and as a disinfectant. Its alcoholic solution is lævo-rotatory.

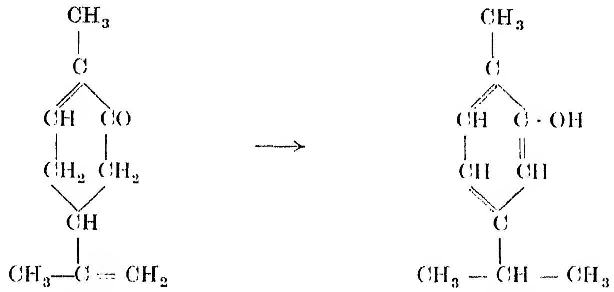
MENTHONE (3-Terpanone or 3-Menthanone), $C_{10}H_{18}O$, is formed by oxidation of menthol with bichromate and sulphuric acid and yields menthol again when reduced with sodium. It is also found in peppermint oil and is a liquid, b.-pt. 207°, with a delicate peppermint odour. It may be converted into thymol.

PULEGONE ($\Delta^{4(8)}$-Terpen-3-one), $C_{10}H_{16}O$, predominates in oil of pennyroyal (*Mentha pulegium*). It is a ketone boiling at 222°, and on reduction gives menthol, so that the carbonyl group is in position 3.

CARVONE (Carvol or Terpadien-2-one), $C_{10}H_{14}O$, is a ketone giving **Carvoxime**, $C_{10}H_{14}$: NOH, which exists in optical isomerides and is identical with nitrosolimonene. It forms

[1] Ciamician and Silber (1910) showed that, in alcoholic solution and under the action of light, menthone is hydrolysed with formation of decoic acid, and an aldehyde isomeric with *citronellal* (p. 252).

the principal component of cumin oil, boils at 228°, and is converted into **Carvacrol**, $C_{10}H_{13} \cdot OH$, when heated with potash or phosphoric acid:

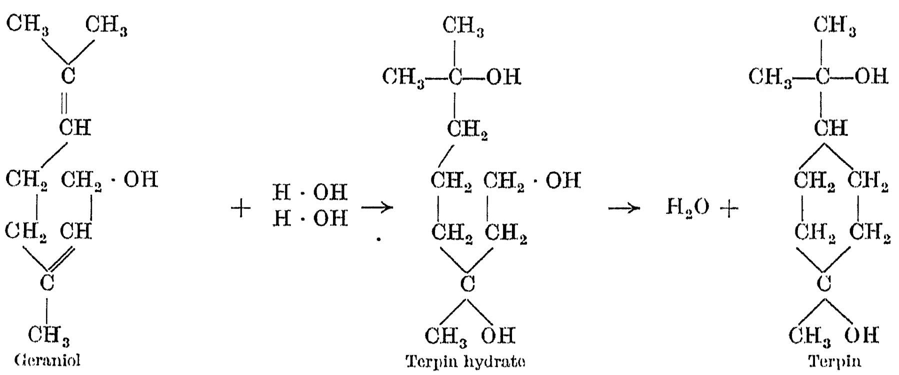


Carvone Carvacrol

TERPENOL ($\Delta^{4(8)}$-Terpen-1-ol), $C_{10}H_{18}O$, melts at 70°, and, like tetramethylethylene, forms a solid blue nitrosochloride, the double linking being in the 4(8)-position, between two tertiary carbon atoms.

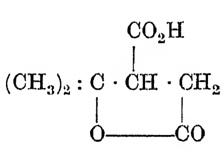
TERPINEOL (Δ^1-Terpen-8-ol), $C_{10}H_{18}O$, melts at 35°, boils at 218°, and is known in the form of various optically active isomerides. It has a pleasing odour of lily of the valley, lilac and cyclamen, and occurs in ethereal oils. With sulphuric acid it forms terpin hydrate, which is also converted back into terpineol by sulphuric acid.

TERPIN (1 : 8-Terpandiol), $C_{10}H_{18}(OH)_2$. Terpin hydrate, $C_{10}H_{20}O_2,H_2O$, is slowly formed from oil of turpentine, $C_{10}H_{16}$, in contact with dilute nitric acid and alcohol. This crystalline hydrate melts at 117° and then loses 1 mol. of H_2O, anhydrous terpin distilling over at 258°. This is optically inactive and is not obtainable in active modifications, so that the presence of asymmetric carbon atoms is excluded. The hydrate is obtainable also from geraniol by the prolonged action of 5 per cent. sulphuric acid, $2H_2O$ being added at the double linkings:



Geraniol Terpin hydrate Terpin

Nitric acid oxidises terpin, giving **Terebic Acid**, which has the known constitution:



so that the position 8 must be occupied by a hydroxyl; the other hydroxyl can only be in position 1, since otherwise an asymmetric carbon atom would be obtained.

CINEOL, $C_{10}H_{18}O$, has the constitution of terpin less H_2O, which is eliminated from the two hydroxyls, an atom of oxygen thus remaining united to the two carbon atoms 1 and 8. Cineol melts at — 1°, boils at 176° and occurs in abundance in eucalyptus oil and in oil of wormseed.

FENCHONE, $C_{10}H_{16}O$. The dextro-form occurs in fennel oil and the lævo in thuja oil. It is a ketone similar to camphor and can be converted into **Fenchene**.

CAMPHOR (*ordinary camphor, laurel camphor*, or **Japan Camphor**), $C_{10}H_{16}O$, is the constituent which separates in the solid form from the essential oil of *Laurus camphora*, a tree which is cultivated in China, Japan, and Formosa, and grows well in Southern Europe (Italy).

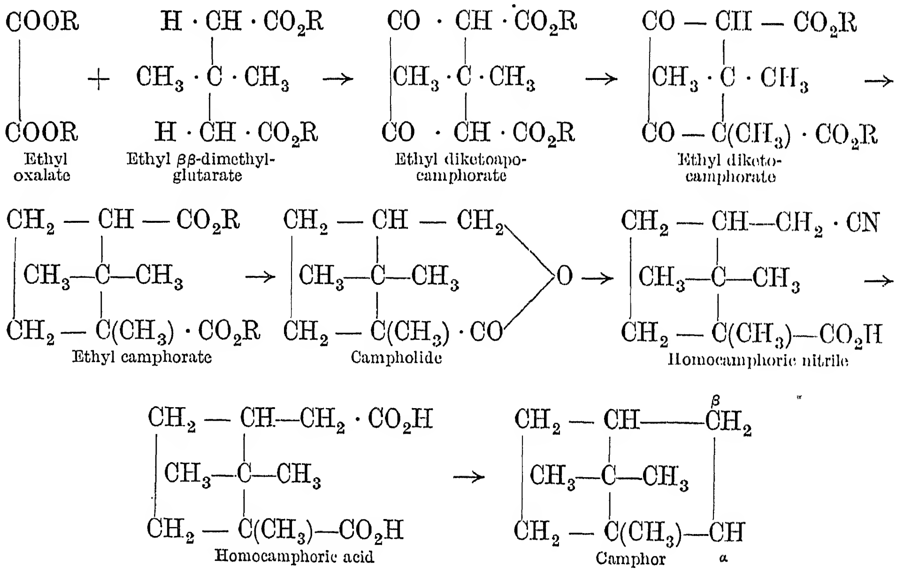
The wood (thirty to forty years old) is chopped up and boiled with water until the camphor floats at the surface; on cooling, the crude camphor sets to a solid mass, which can readily be separated. In some cases the camphor is distilled directly from the wood in a current of steam. The yield is about 1 kilo per quintal of wood. The crude product is refined by mixing with quick-lime and charcoal and subliming at a gentle heat.

It is obtained thus as a white, crystalline, and not very hard mass, which has a characteristic odour, and partially sublimes at the ordinary temperature. It melts at 178°, boils at 207°, and has the sp. gr. 0·922–0·995 (the finer Borneo camphor has sp. gr. 1·10). In alcoholic solution it is more or less dextro-rotatory, according to its origin, but *matricaria camphor* (from the leaves of feverfew, *Matricaria parthenium*) is lævo-rotatory.

With iodine in the hot it forms carvacrol (*see above*), while oxidation with nitric acid gives **Camphoric Acid**, $C_8H_{14}(CO_2H_2)$, which exists in two active and two inactive forms. Further oxidation yields **Camphoronic Acid**, $C_9H_{14}O_6$, which gives trimethylsuccinic acid on dry distillation. When distilled with P_2O_5, camphor loses H_2O and forms cymene. On reduction with nascent hydrogen, ordinary camphor gives **Borneol** (*Borneo camphor*), $C_{10}H_{17} \cdot OH$, which melts at 208°, boils at 212°, and when oxidised gives ordinary camphor, which it strongly resembles.

Between 1860 and 1893 various constitutional formulæ for camphor were proposed by Kekulé, Armstrong, Bredt (1884), and G. Oddo (1891), the last of whom gave a formula which explained well all the reactions and properties observed up to that time. More and more acceptable constitutions were given by Widmann (1891), Collie (1892), Bouveault (1892), etc., and finally by Bredt (1893).

The *constitution* of camphor now seems to be definitely established as the result of various syntheses, especially that from ethyl oxalate and ethyl $\beta\beta$-dimethylglutarate, two compounds which are obtainable synthetically from their elements. The various stages in this synthesis are as follow, R indicating the alkyl group:



This constitutional formula proposed for α-camphor by Bredt, although still contested, is the one generally accepted by chemists, since it corresponds best with most of the reactions of camphor. In 1911, Bredt and Hilbing prepared *β-camphor*, containing the CO group in the β-position, from *bornylenecarboxylic acid*; it melts at 182° and boils at 213·4°.

Camphor forms strongly rotating energetic sulphonic acids, *e.g.*,

$$C_8H_{14}\left\langle\begin{array}{l}CH\cdot SO_3H\\ \,|\\ CO\end{array}\right.$$

, which are able to resolve many racemic compounds into their active components.

Owing to the continually increasing demand for camphor, especially for making *celluloid*,[1] and since many terpenes give camphor when oxidised, many attempts have been made to prepare *artificial camphor* from oil of turpentine. The latter contains pinene, $C_{10}H_{16}$, which is readily convertible into borneol, $C_{10}H_{17}\cdot OH$, or isoborneol, this giving the inactive racemic compound corresponding with natural camphor on oxidation.

According to Ger. Pat. 134,553, when anhydrous turpentine is heated for a long time at 120° to 130° with dry oxalic acid, a mixture of camphor with pinyl formate and oxalate is obtained; after washing with water, the latter are hydrolysed with alkali and the resultant borneol converted into camphor by oxidation with dichromate and sulphuric acid.

At Monville, near Rouen, a factory was erected in 1906 to manufacture artificial camphor by the process described in Fr. Pat. 349,896 (of Béhal, Magnier, and Tissier, and similar to U.S. Pat. 779,377): A mixture of oil of turpentine and salicylic acid is heated and, after elimination of the excess of the reagents, the isoborneol ether is hydrolysed to a mixture of borneol and isoborneol. Another factory, near Calais, utilises Schering's method (Fr. Pat. 341,513), already in use on a large scale in Berlin, and also applied in a factory established in 1909 in Finland.

According to Fr. Pat. 349,852, pinene hydrochloride is first prepared and then heated under pressure with lead acetate in acetic acid solution, thus giving camphene, which with permanganate forms camphor; or treatment of the pinene hydrochloride with a formate gives the formic ester of borneol, which can be readily hydrolysed. The final oxidation to obtain camphor is carried out in various ways: by oxidising the borneol, in benzene or petroleum ether solution, with aqueous alkaline permanganate (Ger. Pat. 157,590), or by means of ozone, air, or chlorine water (*see* Eng. Pat. 28,036 of 1907 and Ger. Pats. 166,722

[1] CELLULOID is obtained by mixing nitrocellulose and camphor in the following manner: well-stabilised, powdered, and partially dried collodion-cotton (with 10 to 11 per cent. N; *see* p. 294) is soaked in alcohol in a covered centrifuge, then gelatinised with alcohol and one-third or one-fourth of its weight of camphor, coloured, if necessary, homogenised between rolls and then formed into dense, compact blocks by pressing while hot. It is then ready to be cut, sawn, compressed, polished, etc., its marked plasticity when hot being utilised in working it. It is a homogeneous, transparent, colourless, or yellowish substance without taste and of sp. gr. 1·37. If sufficiently dry it is odourless, but, when rubbed or heated, it develops a slight smell of camphor. It is a very bad conductor of heat and electricity, and its elasticity is about equal to that of ivory.

Celluloid is used for making toys, balls, combs, walking-stick handles, tortoiseshell objects (substitutes for tortoiseshell, amber, ebonite, etc.), films, etc. It has the disadvantage of burning rapidly and energetically (without exploding) when brought into contact with an ignited or incandescent body. If the collodion-cotton used is well stabilised, celluloid will withstand a temperature of 125° or even higher. It can be charged with mineral substances to render it less inflammable and heavier.

ARTIFICIAL LEATHERS. Celluloid is used to some extent in making artificial leather, the commonest types of these being: (1) *Pegamoid*. This is obtained by spreading on cotton fabrics a solution of celluloid in ethyl or methyl alcohol mixed with castor oil so as to form a soft, elastic paste, which may be coloured by aniline dyes or pigments. By means of incised rollers imitations of different leathers may be obtained. A substitute for pegamoid may be made by spreading on the fabric a dense glue solution and then treating the surface with formaldehyde solution, which renders the glue consistent and insoluble; the surface may afterwards be made shiny with a thin layer of celluloid or cellite (*see* p. 599). (2) *Artificial leather*, made by pressing between rollers several layers of fabric impregnated with glue or, better, rubber solution. Artificial leather is also made by reducing scrap leather to fibre, incorporating it, either alone or mixed with other animal or vegetable fibre, with a little boiled linseed oil, and compressing it into sheets, which may finally be varnished.

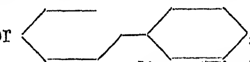
and 154,107), or by oxidising isoborneol in aqueous acid solution with permanganate (Ger. Pat. 197,161 of 1906).

Camphor was obtained by A. Hesse by means of the Grignard reaction, and it is also formed by fusing borneol with finely divided nickel (1911).[1]

Natural camphor may be distinguished from the artificial product by mixing it intimately with an equal weight of chloral hydrate: the former gives a syrupy mass, but the latter does not liquefy. Also with vanillin sulphate or hydrochloride the two give different colour reactions. About 13 per cent. of the total output of camphor is used for pharmaceutical purposes, 15 per cent. for fireworks, nightlights, etc., 70 per cent. for making celluloid, and about 2 per cent. for rendering explosives insensitive to shock.

O. CONDENSED BENZENE NUCLEI

1. DIPHENYL AND ITS DERIVATIVES

DIPHENYL, $C_6H_5 \cdot C_6H_5$, or , is formed by treating an ethereal solution of bromobenzene with sodium (Fittig), by the transformation of hydrazobenzene, or by diazotising benzidine and decomposing the resultant product. It can also be obtained by passing benzene vapour through a red-hot tube.

It forms colourless crystals melting at 71° and boiling at 254°, and is soluble in alcohol and in ether. On oxidation with chromic acid, it gives benzoic acid, its constitution being thus confirmed.

Of *monosubstituted* products of diphenyl, three isomerides are possible, corresponding with the *o*-, *m*-, and *p*-positions with respect to the carbon joined to the second nucleus. Disubstituted derivatives exist in numerous isomeric forms, as the substitution may occur in only one nucleus or in both; in general, however, the substituents enter preferably the para-positions.

BENZIDINE (*p* : *p*-**Diaminodiphenyl**), $NH_2 \cdot C_6H_4 \cdot C_6H_4 \cdot NH_2$. Nitration of diphenyl yields *p* : *p*-dinitrodiphenyl, which, when reduced with zinc dust in alkaline solution, gives benzidine. The latter may also be obtained by electrolysis of nitrobenzene; *see also* Ger. Pat. 122,046, according to which azobenzene is electrolysed in hydrochloric acid solution in presence of stannous chloride.

When pure, benzidine forms colourless scales melting at 122° and then subliming. It dissolves slightly in cold water, but readily in hot water, ether or alcohol. It is a diacid base and gives a sulphate, $C_{12}H_8(NH_2)_2$, H_2SO_4, almost insoluble in water.

It is largely used in making *substantive* dyestuffs (such as *Congo red* and *chrysamine*, which dye cotton without mordants), being first diazotised and then combined with naphthylamine or naphthalenesulphonic acids.

Crude benzidine cost before the war less than 2*s*. 6*d*. per kilo and the pure product 40*s*. The crude sulphate in paste (63 per cent.) cost 2*s*. per kilo and the pure 28*s*.

A higher homologue of benzidine is *o*-**Tolidine**, $C_{12}H_6(CH_3)_2(NH_2)_2$, which

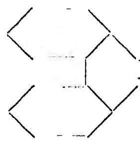
[1] **ARTIFICIAL CAMPHOR.** Before the European War it was noticed that a difficulty might be placed in the way of the further development of the artificial camphor industry by the excessive price of oil of turpentine, this having risen from 56*s*. per quintal in 1900 to 96*s*. in 1906; these conditions might easily be aggravated by the formation of a trust. Further, the demand for camphor may diminish in the future, since substitutes are continually being found capable of replacing it in celluloid, which up to the present has consumed about two-thirds of the total camphor produced. The fact that natural camphor—almost entirely monopolised by the Japanese Government—can be sold, without loss, at 144*s*. per quintal constitutes a menace to the future of artificial camphor, which could never be sold at that price and depends on a raw material the price of which cannot be regulated.

Since the war, however, conditions have radically changed, and if the high price of camphor does not return to a more normal figure, the production of both natural and artificial camphor may be stimulated.

melts at 128°, and the diazo-compound of which combines with naphthionic acid to form a red substantive dyestuff, *benzopurpurine 4B*. The dimethoxy-compound, $(O \cdot CH_3)_2$, of tolidine is *dianisidine*, which with α-naphthol-α-sulphonic acid forms *benzoazurine G* (substantive blue).

CARBAZOLE, $\begin{array}{l} C_6H_4 \\ | \\ C_6H_4 \end{array}\!\!\!>\!NH$, is found in coal-tar, and can be obtained synthetically by distilling *o*-aminodiphenyl over red-hot lime or by gently heating diphenylamine vapour.

The unions of the nitrogen with the two phenyl groups are in the diortho-positions,



so that carbazole may be regarded as a pyrrole derivative (*see later*). It forms colourless scales melting at 238° and readily subliming, and it dissolves in concentrated sulphuric acid, giving a yellow coloration.

From diphenyl can be derived: four isomeric **dihydroxydiphenyls,** $C_{12}H_8(OH)_2$; the **diphenylsulphonic acids**; **diphenyl oxide,** $(C_6H_4)_2O$; **hexa-hydroxydiphenyl,** $C_{12}H_8(OH)_6$ (the mother-substance of cærulignone); and the **diphenylcarboxylic acids** (the di-*p*-acid is a white powder, insoluble in water, alcohol or ether; the di-*o*-acid is **diphenic acid,** $CO_2H \cdot C_6H_4 \cdot C_6H_4 \cdot CO_2H$, m.-pt. 229°) which give diphenyl when heated with lime.

2. DIPHENYLMETHANE AND ITS DERIVATIVES

These compounds may be obtained by condensing either 2 mols. of benzene (or its homologues) with one of methylene chloride, or 1 mol. of benzyl chloride (or benzoyl chloride) with one of benzene (or its homologues or derivatives) in presence of aluminium chloride:

$$2C_6H_6 + CH_2Cl_2 = 2HCl + C_6H_5 \cdot CH_2 \cdot C_6H_5$$
$$C_6H_6 + C_6H_5 \cdot CH_2 \cdot Cl = HCl + C_6H_5 \cdot CH_2 \cdot C_6H_5.$$

Condensation of 2 mols. of benzene with aldehydes (Baeyer) or 1 mol. of an aromatic alcohol with 1 of benzene (V. Meyer) under the influence of concentrated sulphuric acid (ketones, phenols, tertiary anilines, etc., also act similarly):

$$2C_6H_6 + CH_3 \cdot CHO = H_2O + CH_3 \vdots CH(C_6H_5)_2$$
$$C_6H_6 + C_6H_5 \cdot CH_2 \cdot OH = H_2O + C_6H_5 \cdot CH_2 \cdot C_6H_5.$$

DIPHENYLMETHANE, $C_6H_5 \cdot CH_2 \cdot C_6H_5$, forms white crystals melting at 26° and boiling at 262°, has a smell of oranges and is soluble in alcohol or in ether. It is obtained synthetically (*see above*). With water at 150°, its bromo-derivative, $CHBr(C_6H_5)_2$, is converted into **benzhydrol** (*diphenylcarbinol*), $(C_6H_5)_2CH \cdot OH$, which is also obtained on reducing benzophenone.

***p*-Diaminodiphenylmethane,** $CH_2(C_6H_4 \cdot NH_2)_2$, and **tetramethyldiamino-benzhydrol,** $OH \cdot CH[C_6H_4 \cdot N(CH_3)_2]_2$, the latter obtained by reducing Michler's ketone (*see below*) in alkaline solution, are used in the preparation of dyestuffs.

TETRAMETHYLDIAMINODIPHENYLMETHANE or **tetramethyl base,** $CH_2[C_6H_4N(CH_3)_2]_2$, is used in making dyestuffs and serves also as an excellent reagent for detecting small amounts of lead, manganese, ozone, gold, etc., with which it gives characteristic colorations.

BENZOPHENONE (Diphenylketone), $C_6H_5 \cdot CO \cdot C_6H_5$ (*see* p. 675).

TETRAMETHYLDIAMINOBENZOPHENONE or **Michler's ketone,** $CO[C_6H_4N(CH_3)_2]_2$, is prepared by treating dimethylaniline with carbon

oxychloride, heating the resulting dimethyl-*p*-aminobenzoyl chloride in an autoclave with water, removing residual dimethylaniline by steam distillation, dissolving in dilute hydrochloric acid and precipitating the ketone from the filtered solution by means of sodium hydroxide. The crude ketone, after purification, melts at 174°. It may be obtained also by heating together dimethylaminobenzanilide, dimethylaniline and phosphorus chloride. When treated with phosphoryl chloride, it yields the corresponding chloride. With ammonia Michler's ketone gives *auramine*; with diethylaniline, *ethyl violet*; with benzylmethylaniline, *acid violet 4BN*; and with β-naphthol, *wool green S*, etc.

o-**DIHYDROXYBENZOPHENONE**, $[C_6H_4(OH)]_2CO$, by the elimination of a molecule of water from the two hydroxyls, gives **xanthone**, $C_6H_4<\genfrac{}{}{0pt}{}{CO}{O}>C_6H_4$. *p*-**Dihydroxybenzophenone** is obtained from anisaldehyde, so that the hydroxyl groups must be in the para-positions. **Trihydroxybenzophenone** is formed by the condensation of benzoic acid with pyrogallol in presence of zinc chloride. It is used in dyeing under the name *alizarin yellow C* (*see* Dyestuffs).

Other higher derivatives of diphenylmethane are as follow:

as-**DIPHENYLETHANE** (*see later* symm.dibenzyl) is liquid and is formed from paraldehyde and benzene (*see above*). **Benzilic acid** (*diphenylglycollic acid*), $(C_6H_5)_2C(OH) \cdot CO_2H$, is a solid and is obtained by the action of KOH on benzil; by reduction with HI it gives **diphenylacetic acid**, $(C_6H_5)_2CH \cdot CO_2H$.

Tolylphenylmethane, $C_6H_5 \cdot CH_2 \cdot C_6H_4 \cdot CH_3$, exists in several isomeric forms.

Tolyl phenyl ketones, $C_6H_5 \cdot CO \cdot C_6H_4 \cdot CH_3$. The stereoisomeric oximes of these ketones were employed by Hantzsch in developing the stereochemistry of nitrogen (*see* pp. 22, 253).

Benzoylbenzoic Acids, $C_6H_5 \cdot CO \cdot C_6H_4 \cdot CO_2H$: the ortho-acid gives anthraquinone when heated at 180° with P_2O_5.

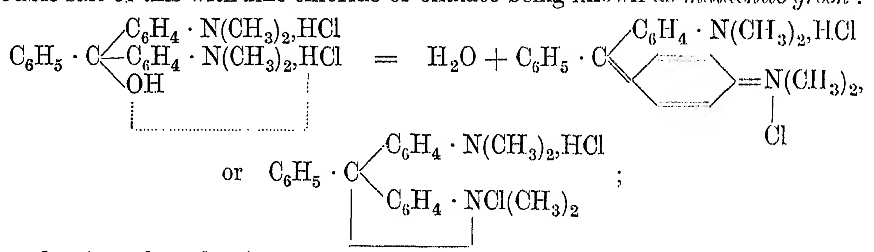
FLUORENE (Diphenylenemethane), $\left|\genfrac{}{}{0pt}{}{C_6H_4}{C_6H_4}\right>CH_2$, is found in coal-tar, and is formed on heating diphenylmethane vapour. It melts at 113°, boils at 295°, and forms scales showing a violet fluorescence.

3. TRIPHENYLMETHANE AND ITS DERIVATIVES

These are prepared synthetically by processes analogous to those used for diphenylmethane, but under such conditions as to lead to the condensation of three benzene nuclei in the methane molecule. The action of chloroform on benzene in presence of $AlCl_3$ gives **TRIPHENYLMETHANE** (m.-pt. 93°; b.-pt. 359°);

$$CHCl_3 + 3C_6H_6 = 3HCl + CH(C_6H_5)_3.$$

The condensation of benzaldehyde and dimethylaniline yields **tetramethyldiaminotriphenylmethane**, $C_6H_5 \cdot CH[C_6H_4 \cdot N(CH_3)_2]_2$, which is a *leuco-base* (*see* Dyestuffs) of malachite green; phenols, etc., condense similarly. When this colourless leuco-base is oxidised with PbO_2 and HCl, it gives **tetramethyldiaminotriphenylcarbinol**, $C_6H_5 \cdot C(OH)[C_6H_4N(CH_3)_2]_2$, which is also a colourless base and forms colourless salts. When, however, these salts are heated in solution, they lose water and form an intense green *colouring-matter*, the double salt of this with zinc chloride or oxalate being known as *malachite green*:



on reduction, the colouring-matter (+ 2H) gives the leuco-base again.

PARAROSANILINE is obtained by oxidising 1 grm. mol. of *p*-toluidine and 2 grm. mols. of aniline with arsenic acid or nitrobenzene. The methyl of the toluidine furnishes the carbon atom for the methane nucleus:

$$CH_3 \cdot C_6H_4 \cdot NH_2 + 2C_6H_5 \cdot NH_2 + 3O = 2H_2O + OH \cdot C \begin{array}{l} C_6H_4 \cdot NH_2 \\ C_6H_4 \cdot NH_2 \\ C_6H_4 \cdot NH_2 \end{array} \text{(base)}.$$

With acids, this base gives a red colouring matter which is precipitated by alkali. When reduced with zinc and hydrochloric acid it yields *paraleucaniline* $HC(C_6H_4 \cdot NH_2)_3$, in colourless crystals which give the coloured base again on oxidation.

Elimination of the amino groups by diazotisation leads to *triphenylmethane*, while nitration of the latter, followed by reduction, gives paraleucaniline, which yields *triaminotriphenylcarbinol* on oxidation. When treated with acids the latter loses H_2O, giving the colouring matter:

$$OH \cdot C \begin{array}{l} (C_6H_4 \cdot NH_2)_2 \\ \\ C_6H_4 \cdot NH_2,HCl \end{array} = H_2O + CCl \begin{array}{l} (C_6H_4 \cdot NH_2)_2 \\ \\ C_6H_4 \cdot NH_2 \end{array}$$

ROSANILINE is formed by oxidising a mixture of *o*- and *p*-toluidines and aniline with arsenious anhydride, mercuric nitrate, or nitrobenzene, the carbon of the methane nucleus being furnished in this case also by the *p*-toluidine:

$$C_6H_4 \begin{array}{l} CH_3 \\ NH_2 \end{array} (p) + C_6H_4 \begin{array}{l} CH_3 \\ NH_2 \end{array} (o) + C_6H_5 \cdot NH_2 + 3O$$

$$= 2H_2O + OH \cdot C \begin{array}{l} C_6H_3 < \begin{array}{l} CH_3 \\ NH_2 \end{array} (o) \\ (C_6H_4 \cdot NH_2)_2 \end{array}$$

Rosaniline hydrochloride (with 1 HCl) or *fuchsine* forms crystals with a green metallic lustre, while the aqueous solution is red owing to the presence of the monovalent cation, $C_{19}H_{18}N_3$, the salt being almost completely ionised.

All fuchsine salts, at the same dilution, give the same absorption spectrum, as they contain the same cation.

If 3HCl are combined, the salts become yellow (yellow trivalent cation); indeed, with excess of HCl fuchsine is almost decolorised, although in dilute solution the red cation is again formed by dissociation.[1]

Replacement of the hydrogen atoms of the amino groups by alkyl groups gives various colouring matters, the intensity of the violet colour increasing with the number of methyl groups.

Pentamethylpararosaniline is the *methyl violet* of commerce.

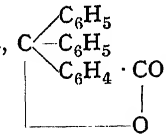
ROSOLIC ACID and AURIN are the phenolic compounds corresponding with rosaniline and pararosaniline, from the diazo compounds of which they are obtained by boiling with water:

$$\underset{\text{Rosolic acid}}{C \begin{array}{l} C_6H_3(OH) \cdot CH_3 \\ C_6H_4 \cdot OH \\ C_6H_4 : O \end{array}} \qquad \qquad \underset{\text{Aurin}}{C \begin{array}{l} (C_6H_4 \cdot OH)_2 \\ \\ C_6H_4 : O \end{array}}$$

[1] It is commonly thought that in the hydrochloride the chlorine is joined to the amino group and not to the carbon of the methane, since, as Tortelli showed (1895), all the chlorine is precipitable by silver nitrate; the compound is hence a salt and not an ether. It cannot, however, be denied that there are compounds, such as *triphenylmethyl chloride*, $(C_6H_5)_3C \cdot Cl$, which behave similarly, being hydrolysable by water and then completely precipitable by silver nitrate. Then, too, *methyl iodide* is hydrolysed by water alone to the extent of 0·6 per cent. in 13 hours, whilst in the presence of silver nitrate 96 per cent. of the iodide is hydrolysed in the same time. It is hence more accurate to state that, after hydrolysis, these ethereal compounds behave like salts.

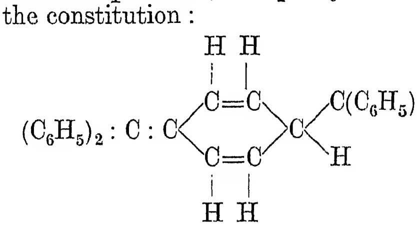
Rosenstiehl maintains that every double decomposition between *salts* (especially organic) is preceded by hydrolysis, and those salts and ethereal compounds which hydrolyse slowly he calls *bradolytes*, and those which hydrolyse rapidly, *stenolytes*.

They are colouring-matters of an acid character and of but little importance, and they form dark red prisms with a greenish, metallic reflection.

PHTHALOPHENONE,  , may be regarded as a derivative of phthalic acid (*see* p. 684) or of triphenylmethane.

It is the anhydride of triphenylcarbinol-*o*-carboxylic acid, $C(OH)(C_6H_5)_2(C_6H_4 \cdot CO_2H)$, and is obtained by heating phthalyl chloride with benzene in presence of aluminium chloride. It forms scales melting at 115° and dissolves in alkali giving a salt of the acid, the latter not being obtainable in the free state. Its phenolic derivatives are the *phthaleins* (*see* p. 685).

HEXAPHENYLETHANE, $(C_6H_5)_3C \cdot C(C_6H_5)_3$, is of some interest theoretically, as its molecule was at first regarded as $C(C_6H_5)_3$ (**Triphenylmethyl**) and was looked upon as the first example of an organic compound containing trivalent carbon, but cryoscopic examination shows that it has the doubled molecular weight, and hence indicates the constitution $(C_6H_5)_3C \cdot C(C_6H_5)_3$. It was prepared by Gomberg by the action of zinc on triphenylchloromethane, and is a solid, stable substance which, in solution, has a yellow colour and becomes unstable owing to its great power of reacting; with the oxygen of the air it forms a peroxide, $(C_6H_5)_3 \cdot C \cdot O \cdot O \cdot C(C_6H_5)_3$. On account of the facility with which it forms additive products, hexaphenylethane is regarded by some as having in solution the constitution :



An analogous compound is **Pentaphenylethane,** $(C_6H_5)_3C \cdot CH(C_6H_5)_2$, stable at the ordinary temperature but not in the hot.

4. DIBENZYL AND ITS DERIVATIVES

The constitution of these compounds is shown by their methods of synthesis and by the fact that they all yield benzoic acid on oxidation.

DIBENZYL (*symm.* **Diphenylethane**), $C_6H_5 \cdot CH_2 \cdot CH_2 \cdot C_6H_5$, is obtained from benzyl chloride and sodium :

$$2C_6H_5 \cdot CH_2 \cdot Cl + Na_2 = 2NaCl + C_6H_5 \cdot CH_2 \cdot CH_2 \cdot C_6H_5 :$$

it melts at 52°.

STILBENE (*symm.* **Diphenylethylene**), $C_6H_5 \cdot CH : CH \cdot C_6H_5$, melts at 125°, and is obtained from benzal chloride (benzylidene chloride) and sodium. Owing to its double linking, it can unite with two atoms of Br, which can be eliminated as HBr by treatment with alcoholic potash, the resulting product being **TOLANE** (**diphenylacetylene**), $C_6H_5 \cdot C \vdots C \cdot C_6H_5$, melting at 60°, and behaving like an acetylene derivative.

p-**DIAMINOSTILBENE,** $NH_2 \cdot C_6H_4 \cdot CH : CH \cdot C_6H_4 \cdot NH_2$, is used, especially in the form of the corresponding sulphonic acids, for the preparation of various substantive dyestuffs.

BENZOIN, $C_6H_5 \cdot CH(OH) \cdot CO \cdot C_6H_5$, is formed by oxidising **HYDROBENZOIN,** $C_6H_5 \cdot CH(OH) \cdot CH(OH) \cdot C_6H_5$, which is obtained by treating benzaldehyde with sodium amalgam. Benzoin exists in two stereoisomeric modifications, melting at 138° and 119°. It reduces Fehling's solution even in the cold (giving benzil) and forms a phenylosazone, since it contains, like the sugars, the group $\cdot CO \cdot CH(OH)$.

BENZIL, $C_6H_5 \cdot CO \cdot CO \cdot C_6H_5$, is a yellow diketone and forms three benzildioximes (*see* pp. 22, 253).

$$\begin{array}{ccc} C_6H_5 \cdot C\text{———}C \cdot C_6H_5 & C_6H_5 \cdot C\text{———}C \cdot C_6H_5 & C_6H_5 \cdot C\text{————}C \cdot C_6H_5 \\ \quad\ \ \| \qquad\quad \| & \quad\ \ \| \qquad\quad \| & \quad\ \ \| \qquad\quad \| \\ N \cdot OH \quad N \cdot OH & OH \cdot N \quad\ N \cdot OH & N \cdot OH \quad OH \cdot N \\ \textit{Amphi-benzildioxime} & \textit{Anti-benzildioxime} & \textit{Syn-benzildioxime} \end{array}$$

When heated with alcoholic potash, benzil combines with H_2O, giving benzylic acid:

$$C_6H_5 \cdot CO \cdot CO \cdot C_6H_5 + H \cdot OH = (C_6H_5)_2C{<}^{CO_2H}_{OH}$$

DESOXYBENZOIN, $C_6H_5 \cdot CH_2 \cdot CO \cdot C_6H_5$, is obtained from phenylacetyl chloride, $C_6H_5 \cdot CH_2 \cdot CO \cdot Cl$, and benzene in presence of aluminium chloride, and also from benzoin and benzil. It melts at 55° and gives dibenzil when reduced with hydriodic acid.

HEXABENZYLETHANE, $(C_6H_5 \cdot CH_2)_3C \cdot C(CH_2 \cdot C_6H_5)_3$, was prepared by Schmerda (1909) by heating tribenzylcarbinol with hydriodic acid in a sealed tube at 200°, the product being shaken with bisulphite, extracted with ether and the latter distilled off. It forms a yellowish crystalline mass which is recrystallised from acetone and glacial acetic acid; it melts at 80° to 81°. From the mother-liquor dibenzyl is obtained.

5. NAPHTHALENE AND ITS DERIVATIVES

NAPHTHALENE, $C_{10}H_8$, discovered in tar in 1819 and 1821 by Garden and Kitt, occurs in abundance in crude illuminating gas and in coal-tar. When the latter is distilled (*see* pp. 625 *et seq.*), the naphthalene is obtained from the portions distilling between 170° and 230° and by redistilling the residues of the oils from which the carbolic acid has been extracted with caustic soda, care being taken to surround the condenser coils with hot water to prevent stoppages.

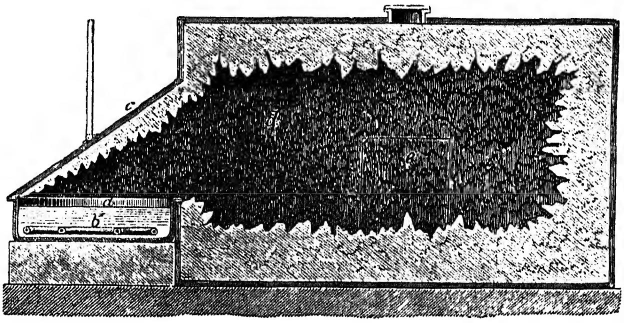


Fig. 464.

The first separation of the naphthalene from the crude oils yielded at various stages of the distillation is effected by cooling in large tanks, crystallised naphthalene separating out.

The oily impurities of the crystals are removed in a hydraulic press with heated plates. Attempts have been made to centrifuge the crude naphthalene, but even when this is steamed in the centrifuge, the residual product is always very impure and unsuitable for distillation or sublimation. In consequence of this, use has been made of hydraulic presses with horizontal rods and vertical plates heated by steam, but these give insufficient pressure and too much waste, and require too much time and attention. The best results are given by presses with vertical colums and ring plates (similar to the presses described on pp. 484, 485), which work continuously and readily attain a pressure of 102 kilos per square centimetre with a diminished consumption of steam. Nowadays hydraulic presses with perforated steel bells are used—similar to those used for oily seeds—and in 10 hours each of these can effect 30 compressions of 100 kilos; when several presses are worked, hydraulic accumulators (*see* p. 484) are used. If well pressed, naphthalene has the mean solidifying point 78·6° and 95·5 per cent. of it distils between 216·5° and 218·5°. Attempts have been made to purify naphthalene with a solution of resin soap, but such a method is too expensive (a centrifuged naphthalene containing 7 per cent. of oil gives, with 5 per cent. of colophony and the corresponding quantity of caustic alkali solution, 85 per cent. of pure naphthalene with the solidifying point 78·8°). The compressed naphthalene is purified further in metal vessels with conical bases and fitted with stirrers (sometimes with air-jets). In these the molten naphthalene is agitated for 15 minutes with 5 per cent. of sulphuric acid of 50° Bé. (already used once) to dry the mass somewhat and free it from

pyridine compounds; after removal of this acid, the mass is shaken successively with 5 to 6 per cent. of sulphuric acid of 60° Bé. for 30 minutes, 4 per cent. of hot water, 4 per cent. of caustic soda solution of 19° Bé. (already used once), and finally, 2 per cent. of hot water. After settling and removal of the water as far as is possible by decantation, the naphthalene is distilled in large stills holding 100 to 150 quintals and furnished with a rectifying column 2 to 3 metres high. Water distils over first and then pure naphthalene, which is collected in metal boxes, allowed to crystallise in moulds and granulated by means of a crusher; the solidifying point is then 70·7°, while 97·5 per cent. distils between 216·6° and 218°.

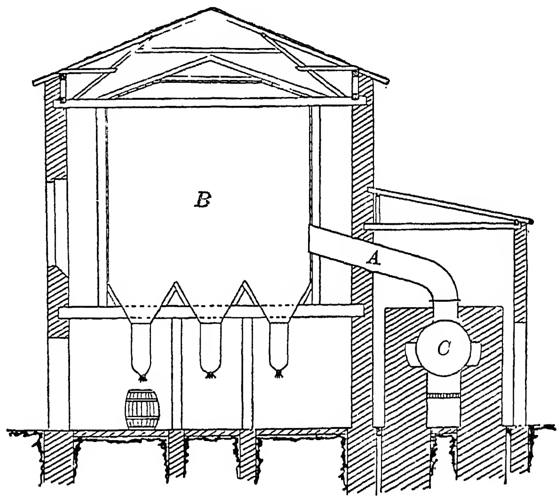


FIG. 465.

A purer product, in the form of large, shining scales, can be obtained by *sublimation* (instead of distillation) in an open vessel, *a* (Fig. 464), having an area of 2 to 3 sq. metres and covered with an inclined wooden plane leading to a large wooden chamber, 20 to 25 cu. metres in capacity. The naphthalene is heated by a pressure steam-coil and sublimes and condenses in the large chamber, forming on the walls a thick layer of shining, white scales of pure naphthalene. In order to avoid loss and to obtain continuous working, the naphthalene is introduced into long cylindrical boilers, bricked in like steam boilers and connected with a large wooden chamber (350 cu. metres, Fig. 465), which has a base fitted with conical outlets leading to sacks for catching the naphthalene as it becomes detached from the walls (these are knocked from time to time). In this way 70 kilos of pure naphthalene are obtained per 12 hours for each 100 cu. metres of capacity.

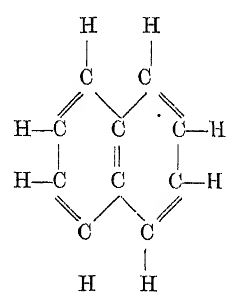
Pure naphthalene forms shining scales melting at 79·6° and boiling at 218°. It is insoluble in water, but dissolves readily in boiling alcohol or in ether; it volatilises even at the ordinary temperature and distils readily in steam.

The calorific value of naphthalene is 6940 cals., and its vapour pressure at different temperatures as follows (mm. of mercury):

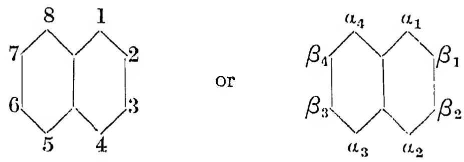
0°	20°	50°	80°	100°	120°	141°	159°	165°
0·022	0·080	0·81	7·4	18·5	40·2	90·4	169	207

Its sp. gr. is 1·152 at 15° and 0·977 at its melting-point. If pure it does not colour concentrated sulphuric acid at 80°.

Constitution of Naphthalene. The following structural formula is attributed to naphthalene:

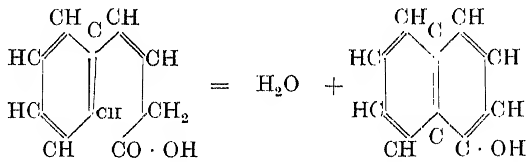


and to indicate the positions occupied by groups replacing the hydrogens in derivatives the carbon atoms are numbered or lettered with Greek letters, thus:

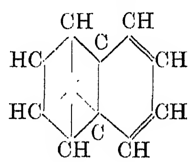


That the two nuclei are united by means of two carbon atoms in the ortho-position is shown by the fact that oxidation of naphthalene in such a way as to destroy one of the nuclei results in the formation of phthalic acid, which is known to contain two carboxyl groups in adjacent positions.

Further, since when phenylisocrotonic acid is heated a naphthalene derivative, namely, α-naphthol, results, it is clear that the second nucleus is formed by the elimination of a molecule of water with closure of the chain of the four carbon atoms of the side-chain of the original acid and two ortho-carbon atoms in the benzene nucleus :



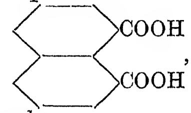
That there are two condensed benzene nuclei is also deduced from the fact that oxidation of α-nitronaphthalene gives nitrophthalic acid, the benzene nucleus containing the nitro-group being preserved and the other destroyed. If, however, the nitro-group is first reduced to an amino-group, oxidation results in the destruction of the nucleus containing the amino-group and in the preservation of the other, phthalic acid, which undoubtedly contains a benzene nucleus, being formed. That the linkings between carbon and carbon are different in the two nuclei is shown by the addition of four hydrogen atoms to one of the nuclei, which probably has true double linkings, while the other nucleus would seem to have a true benzenic character with centric linkings (Bamberger) ; further, the addition of ozone proves with certainty the presence of olefinic double linkings (E. Molinari, 1907) :



USES. Naphthalene is used in large quantities in the preparation of various dyestuffs (eosin, indigo, Martius yellow, tropæolin, Biebrich scarlet, croceine scarlet, etc.), phthalic acid, lampblack, varnishes, and cart-grease, and is employed also as an antiseptic and as a preventative of moth in clothes. For some time it has been mixed with camphor in order to render *celluloid* less inflammable and less explosive.

Crude naphthalene cost before the war 11*s*. to 12*s*. per quintal, while the pure white scales were sold at 16*s*., pure in tapers at 17*s*. 6*d*., and chemically pure at 80*s*. per quintal.

The isomerides of the substitution products of naphthalene are more numerous than in the case of benzene. Thus, there are two isomeric mono-substituted derivatives, the α-compound with the substituent in the 1-, 4-, 5-, or 8-position, and the β-compound with the substituent in the 2-, 3-, 6-, or 7-position. The isomeric disubstituted compounds with two similar substituents are ten in number, while with two different substituting groups fourteen isomerides are possible, and, in some cases, all known.

Compounds with substituents in the 1- and 8- or the 4- and 5-positions are known as $\alpha\alpha$- or *peri*-compounds, *e.g.*, Perinaphthalenedicarboxylic acid,  , which readily forms an anhydride owing to the proximity of the hydroxyls.

The number of isomerides being so large, it is sometimes difficult to determine the constitution of a derivative. To this end the oxidation products are often studied, the forma-

tion of phthalic acid indicating that all the substituents are in the one benzene nucleus destroyed by the oxidation, while the formation of a substituted phthalic acid indicates the opposite to be the case.

α-CHLORONAPHTHALENE, $C_{10}H_7Cl$. Treatment of naphthalene with chlorine yields preferably additive products with two or four chlorine atoms in the same benzene nucleus. On the other hand, the action of chlorine on a cold solution of naphthalene in carbon tetrachloride in presence of a catalyst (*e.g.*, ferric chloride) yields substituted products: α-monochloro-, then 1 : 4- and 1 : 5- and small proportions of 1 : 2- and 1 : 7-dichloronaphthalenes.

Also with boiling naphthalene chlorine forms directly α-chloronaphthalene, but this is obtained in a purer form by diazotising α-naphthylamine and then decomposing with copper chloride (Sandmeyer's reaction, p. 670). It is a liquid of sp. gr. 1·1938, b.-pt. 263°, and forms a yellow, crystalline picrate, m.-pt. 137°. When nitrated it forms mainly 1-chloro-4-nitronaphthalene, together with a little 1 : 5- and 1 : 8-compounds. It serves for making various chlorosulphonic acids and also naphthalene green V, and has been suggested as a lubricant.

Of importance in the explosives industry are various nitro-derivatives of naphthalene, and in the dyestuffs industry, besides nitro-derivatives, also the aminocompounds, and especially the numerous sulphonic derivatives.

α-NITRONAPHTHALENE, $C_{10}H_7 \cdot NO_2$. Of the α- and β-nitronaphthalenes, only the former is of industrial importance, being used for making dinitronaphthalene and particularly α-naphthylamine.

The industrial preparation is carried out in a nitrating vessel (*see* p. 649), 100 kilos of pure ground naphthalene being added rapidly, with stirring, to 300 kilos of 55 per cent. sulphuric acid (45° Bé.), the temperature being raised to 50°; 200 kilos of a mixture containing 26 per cent. of HNO_3, 60 per cent. of H_2SO_4, and 14 per cent. of water is then added slowly, the temperature being raised gradually to 60° and mixing continued for a couple of hours. The residual acid, containing about 63 per cent. of H_2SO_4 and 0·5 per cent. of HNO_3, is then decanted off, and, after dilution to 55 per cent., used for treating a fresh batch of naphthalene. The fused nitronaphthalene is run into a vessel of hot water furnished with a stirrer, and is washed twice with almost boiling water and once with a very dilute sodium carbonate solution, the molten compound being poured into cold water, kept stirred and thus granulated, and then centrifuged and used moist for reduction to α-naphthylamine. It is used also for making 1-nitronaphthalene-5-sulphonic acid, and when fused with sulphur gives blue and green sulphur colouring matters.

When α-nitronaphthalene vapour and hydrogen are passed at 340° over finely divided copper, α-naphthylamine is formed directly, but if the copper is replaced by powdered nickel, tetrahydronaphthalene (and NH_3) is obtained as a secondary product. With sulphites it gives naphthionic and naphthylamine-2 : 4-disulphonic acids, and with chlorine in presence of catalysts at 40° to 60° it forms 1-chloro-5-nitro- and also 1-chloro-8-nitronaphthalenes (Ullmann and Consonno, 1902).

It is used for removing the fluorescence from mineral oils, being stored away from the oil to minimise damage in case of fire.

It is poisonous and forms a yellow, crystalline mass, m.-pt. 61° (the commercial product has m.-pt. 58° to 59°), b.-pt. 304°, and when molten has sp. gr. 1·223. It is insoluble in water, but dissolves in benzene, ether, carbon disulphide or hot alcohol.

The crude product cost 64*s.* to 76*s.* per quintal before the war, and the pure crystals 96*s.*

DINITRONAPHTHALENES, $C_{10}H_6(NO_2)_2$. Nitration of α-nitronaphthalene or direct nitration of naphthalene with a suitable nitric-sulphuric acid mixture yields always a mixture of various dinitronaphthalenes, consisting principally of the 1 : 8- (about 60 per cent.) and the 1 : 5-compound (about 30 per cent.) together with other isomerides and trinitronaphthalene. The mixture may be used directly for explosives (*see* p. 305).

The two dinitro-compounds may be separated by dissolving in hot sulphuric acid of 62° Bé. which, on cooling, deposits the 1 : 5-compound, whilst the 1 : 8-derivative separates at a lower temperature or, better, on slight dilution with water. Also a hot pyridine solution deposits the 1 : 5-compound on cooling, removal of two-thirds of the pyridine by distillation and subsequent cooling resulting in the crystallisation of 1 : 8-derivative.

1 : 5- (or α-) Dinitronaphthalene, which is used for making *naphthazarin black* (*see later*), crystallises in yellowish needles, m.-pt. 214°, and is readily sulphonated by fuming sulphuric acid. When reduced with ammonium sulphide it gives first 1-nitro-5-aminonaph-

thalene and then 1 : 5-naphthylenediamine; when boiled with sodium bisulphite or ammonium sulphite solution it yields 1 : 5-naphthylenediaminedisulphonic acid.

1 : 8- (or β-) Dinitronaphthalene, m.-pt. 172°, is more soluble in various solvents than the 1 : 5-compound. With sodium bisulphite it gives 1 : 8-naphthylenediaminetrisulphonic acid. It behaves like the 1 : 5-isomeride with fuming sulphuric acid and is used for making sulphur blacks and blue.

TRI- and TETRA-NITRONAPHTHALENES are otained by nitrating naphthalene or the mono- and di-nitro-compounds with more concentrated nitric-sulphuric acids and with rather more than the theoretical quantity of nitric acid.

α-NAPHTHYLAMINE (1-Aminonaphthalene), $C_{10}H_7 \cdot NH_2$. The commercial product forms lustrous, square scales with a reddish-brown tint; it contains a little naphthalene and water and has a slight fæcal odour (β-naphthylamine is odourless). The pure, freshly made product is pale pink, melts at 50° and boils at 300·8°. It has no alkaline reaction, and is readily soluble in alcohol, ether, benzene, toluene, etc.; 100 c.c. of water dissolves only 0·167 grm. With oxidising agents such as ferric chloride, chromates, etc., its salts give a blue precipitate of *naphthamine*, changing to purple-red (different from β-naphthylamine); this reaction is used by van Eck (1915) for the colorimetric estimation of chromates.

With $CaCl_2$ or $ZnCl_2$ at 280° it gives a little ammonia and α-dinaphthylamine (*see later*). With sodium nitrite naphthylamine salts in slightly acid solution give a brown precipitate of aminoazonaphthalene, $C_{10}H_7 \cdot N_2 \cdot C_{10}H_6 \cdot NH_2$, and in highly acid solution, α-diazonaphthalene, $C_{10}H_7 \cdot N_2 \cdot X$. On protracted boiling with water it is converted partly into α-naphthol. The *hydrochloride* sublimes at 200°, and the *sulphate* crystallises with $2H_2O$.

α-Naphthylamine is used to make α-naphthol (*see later*), various sulphonic derivatives, numerous azo dyestuffs, and Magdala red. It serves also for many direct diazotisations on cotton fibre, to be coupled with, for instance, β-naphthol to obtain a bluish-red colour (Bordeaux) fast against soap, etc. It is also employed in photography, together with oxidising agents, to obtain bluish tones. Before the war it was sold at about 1*s.* 6*d.* per kilo.

MANUFACTURE. It is usually obtained, similarly to aniline, by reducing α-nitronaphthalene with iron and hydrochloric acid. Electrolytic reduction (Boehringer, Ger. Pat. 116,942) and reduction with hydrogen in presence of a catalyst (*e.g.*, copper), as suggested by Sabatier and Senderens (1902), do not give satisfactory results in practice. It is purified by distillation in a vacuum.

β-NAPHTHYLAMINE. Nitration of naphthalene does not yield β-nitronaphthalene, and β-naphthylamine is obtained by heating β-naphthol (100 grms.) with 150 c.c. of 40 per cent. ammonium sulphite solution and 100 c.c. of 20 per cent. ammonia solution in an autoclave at 140° to 150° until all the β-naphthol has reacted, the slightly cooled mass being filtered by suction, washed with dilute caustic soda, dissolved in tepid dilute hydrochloric acid solution and filtered from insoluble $\beta\beta$-dinaphthylamine. The β-naphthylamine, precipitated by dilute caustic soda, has m.-pt. 112°, b.-pt. 294°. It is used for making β-naphthylaminesulphonic acid and various azo dyestuffs, and costs three times as much as its α-isomeride.

The following are important derivatives of the naphthylamines: (1) **Ethyl-α-naphthylamine**, $C_{10}H_7 \cdot NH \cdot C_2H_5$, is used in making *lanacyl violet B* and *new Victoria blue B*, a basic dyestuff which dyes wool directly and cotton, after mordanting, pure sky blue. (2) **Phenyl-α-naphthylamine**, from aniline and α-naphthylamine at 230° to 250° in presence of iodine, or from aniline hydrochloride and α-naphthol, serves to make *sulphonazurine D*, *jet black R*, etc. (3) **p-Tolyl-α-naphthylamine**, $C_{10}H_7 \cdot NH \cdot C_6H_4 \cdot CH_3$, is used for making *night blue.* The corresponding β-naphthylamine derivatives are used for making: (1) *Developer B* (Bordeaux) for primuline dyestuffs; (2) *night blue*; (3) *wool black.*

α-NAPHTHOL, $C_{10}H_7 \cdot OH$, forms lustrous, monoclinic needles, m.-pt. 94°, b.-pt. 279°, and dissolves in alcohol, ether, benzene, etc., but is insoluble in water. With ferric chloride or a hypochlorite it forms *α-dinaphthol* in blue flocks. When fused with alkali in presence of copper oxide it gives benzoic and phthalic acids. It unites with two molecules of diazonium salts in the o- and p-positions to the hydroxyl. It is used in making numerous azo dyestuffs (brown, black, orange), *indophenol* and, especially, various sulphonic acids as intermediates for important dyestuffs (Martius yellow, naphthol yellow S, etc.). It condenses with Michler's ketone to give indigoid dyestuffs and *naphthol blue.*

PREPARATION. α-Naphthol is obtained pure by heating α-naphthylamine and sul-

phuric acid in a lead-lined or enamelled autoclave at 200° (14 atmos.), the mother liquors yielding ammonium sulphate. The process most commonly used and possibly more economical is the following, which yields α- mixed with a little β-naphthol. Sodium naphthalene-α-sulphonate is first prepared by heating naphthalene with sulphuric acid and pouring the mass into sodium sulphate solution. This salt is pressed hydraulically under 200 atmos. pressure so that a product with only about 15 per cent. of water is obtained, this being fused with commercial caustic soda and a little water and the mass poured into cold water, which is subsequently neutralised with sulphuric acid. The α-naphthol crystals are pressed, fused to eliminate water, and distilled under a pressure of 50 mm. at a temperature of about 165°.

β-NAPHTHOL forms lustrous white crystals, m.-pt. 123°, b.-pt. 285°, sublimes readily and distils well in superheated steam. It dissolves in 5000 parts of cold or 75 of boiling water, and is readily soluble in alcohol, ether, benzene, etc. With ferric chloride it gives a greenish coloration and afterwards white flocks of $\beta:\beta$-dinaphthol. When oxidised in alkaline solution with potassium permanganate it yields *o*-carboxycinnamic acid, and when fused with caustic soda in presence of copper oxide, phthalic and benzoic acids.

It is used in making numerous dyestuffs, especially of the azo group, since it may be coupled in many different ways (orange II, paranitraniline red, various ponceaus and scarlets for wool and for silk, dianisidine blue, greens, blacks, etc., etc.). It is used also as a disinfectant in skin diseases, and its methyl and ethyl esters form fruit essences.

PREPARATION. Industrially it is prepared solely from sodium β-naphthalenesulphonate by a process analogous to that used for making the α-isomeride, special conditions being employed to prevent formation of α-naphthol and disulphonic acids.

Betol or Naphthosalol (the salicylic ester of β-naphthol), $C_{10}H_7 \cdot O \cdot CO \cdot C_6H_4 \cdot OH$, melts at 95°, and is used in medicine under the name of salol.

Neroline, $C_{10}H_7 \cdot OC_2H_5$, is the ethyl (or methyl) ether of β-naphthol and has the same odour as orange flower oil (neroli).

Dihydroxynaphthalenes, $C_{10}H_6(OH)_2$, are known in various isomerides: the 1 : 5-compound, m.-pt. 259°, obtained by the alkaline fusion of sodium naphthalenedisulphonate, serves for making benzidine blue dyestuffs, diamond black PV, etc. The 1 : 8-, 2 : 3- and 2 : 7-isomerides are also used for making azo dyestuffs, etc.

Aminonaphthols, $OH \cdot C_{10}H_6 \cdot NH_2$: the various isomerides are used for preparing dyestuffs.

SULPHONIC DERIVATIVES OF NAPHTHALENE, NAPHTHOLS, AND NAPHTHYLAMINES

These form an important group comprising the principal *intermediates* used in making dyestuffs. Only the more important can be referred to here.

The sulphonation of naphthalene is analogous to that already given for benzene (*see* p. 637) and, since naphthalene sulphonates readily and gives a large number of isomerides, mixtures difficult to separate are often obtained. The α-derivatives are formed preferably at comparatively low temperatures and the β-derivatives at higher temperatures (100° to 200°). Sodium amalgam eliminates α- more readily than β-sulphonic groups.

NAPHTHALENE-α-SULPHONIC ACID, $C_{10}H_7 \cdot SO_3H$, m.-pt. 87°, gives the β-isomeride when heated with concentrated sulphuric acid, dissolves appreciable amounts of phenol, and is used for making α-naphthol.

NAPHTHALENE-β-SULPHONIC ACID serves for making β-naphthol and precipitates proteins in the cold.

1-AMINO-2-NAPHTHOL, $NH_2 \cdot C_{10}H_6 \cdot OH$, is obtained by nitrating β-naphthol ethyl ether and then reducing. The ethyl ether, m.-pt. 51°, is used for making *diamine blue 6G*, *diamond green*, and various bluish naphthyl blacks.

1-NAPHTHOL-2-CARBOXYLIC ACID, obtained like salicylic acid (p. 686) by heating dry sodium α-naphtholate with CO_2 in an autoclave at 130°, is used as an antiseptic and in making *chrome blue*.

2-NAPHTHOL-1-CARBOXYLIC ACID, obtained similarly, melts at 128° to 156° with evolution of CO_2. It is used to replace β-naphthol in making lakes coloured directly on the fibre.

1-NAPHTHOL-4-SULPHONIC ACID, known also as Nevile and Winther's acid or NW acid, forms transparent tubular crystals, melting and generating gas at 170°. It is used in making azo dyestuffs, *e.g.*, azococcine 2R, fast red VR, cloth red G and B, diamond black

F, alizarine bordeaux W, anthracene red, diamond blue 2R, diamine blue BX, benzo-azurine G, etc.

β-**NAPHTHOLSULPHONIC AND DISULPHONIC ACIDS.** Treatment of β-naphthol with sulphuric acid yields various products according to the concentration of the acid and the temperature. Owing to the difficulty of obtaining a single sulphonation product, mixtures of two acids are usually made and then resolved into the components.

2-NAPHTHOL-6-SULPHONIC ACID, or Schäffer's acid, melts at 125°, gives dihydroxy-naphthalene, m.-pt. 213°, when fused with alkali, and is used for making azo dyestuffs: brilliant orange O, fast red BT, bordeaux G, diaminogen blue BB, alizarin acid black SN; the iron salt of the nitroso-derivative forms naphthol green S.

1-NAPHTHOL-5-SULPHONIC ACID, or Cleve's acid, m.-pt. 110° to 120°, obtained by boiling the diazo-derivative of 1-naphthylamine-5-sulphonic acid with water, is used for making cochineal scarlet 4R, diamond black F, benzo azurine 3G, etc.

2-NAPHTHOL-3 : 6-DISULPHONIC ACID (R acid) and **2-NAPHTHOL-6 : 8-DISULPHONIC ACID** (G acid) are obtained by adding finely divided β-naphthol gradually to sulphuric acid (monohydrate), the mixture being kept cold. The G acid is used for making γ-acid. The potassium salts are used for making orange III, alizarin acid red B, Congo blue 2B, naphthol black, diamine scarlet B, etc.

1-NAPHTHOL-3 : 6 : 8-TRISULPHONIC ACID is used in large quantities for making naphthol yellow S.

NAPHTHIONIC ACID or **1-NAPHTHYLAMINE-4-SULPHONIC ACID** is obtained like sulphanilic acid (p. 637) by heating naphthylamine acid sulphate at 180° to 200° and is used in making many azo dyestuffs: naphthylamine brown, azorubine, crocein scarlet, cochineal red, benzo orange, benzo-purpurines 4B and 10B, dianil black, etc. The sodium salt is used in making colloidal gold solutions.

CLEVE'S ACID is the 1 : 7-isomeride, used for Biebrich black.

DAHL'S ACID is 2-naphthylamine-5-sulphonic acid mixed with the 2 : 8-compound and is used for making ponceau for silk G.

DAHL'S ACID II, 1-naphthylamine-4 : 6-disulphonic acid, is used, mixed with Dahl's acid III (2 : 6 : 8), for making various naphthol blue-blacks.

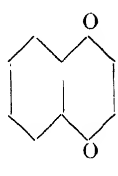
AMINO R ACID, 2-naphthylamine-3 : 6-disulphonic acid, and the isomeric **AMINO ACID G** (2 : 6 : 8), serve for making brilliant crocein, amine blue 6G, naphthol black B, etc.

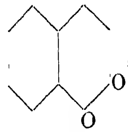
Eikonogen is the sodium salt of α^1-amino-β^1-naphthol-β^2-sulphonic acid and is used as a photographic developer.

γ-**ACID** or 2-amino-8-naphthol-6-sulphonic acid, prepared together with more or less **J-ACID** (2 : 5 : 7), gives two series of azo dyestuffs by coupling with diazo compounds in acid and alkaline solutions and also directly on cotton fibre. It is used for making diamine violet N, diamine blacks, diaminogen blue, dianil black PR, etc., all these for dyeing cotton without mordants.

H-ACID or 1-amino-8-naphthol-3 : 6-disulphonic acid is the most important of the naphthalene sulphonic derivatives and is used in making numerous azo dyestuffs for dyeing cotton without mordants or wool and silk: various diamine blues, naphthylamine black 10B, diamine bronze G, diamine green B, fast acid magenta, lanacyl dyestuffs, etc. Before the war it cost 4*s.* per kilo, and during the war as much as £4.

CHROMOTROPE ACID or 1 : 8-dihydroxynaphthalene-3 : 6-disulphonic acid, obtained by fusing naphthylaminetrisulphonic acid with alkali in an autoclave, is used for making chromotrope blue and black, Victoria violet 4BS, dianil blue, etc.; its sodium salt forms chromogene I.

α-**NAPHTHAQUINONE,** , is obtained in yellow crystals melting at 125° by oxidising naphthalene with chromic acid in boiling acetic acid solution. From its constitution those of other substitution products of naphthalene can be deduced, since, when the substituent groups are in the para-position, oxidation always leads ultimately to α-naphthaquinone. It is volatile in steam.

β-NAPHTHAQUINONE, $C_{10}H_6O_2$ or , is formed by the oxidation of 1 : 2-aminonaphthol, and crystallises in reddish yellow leaflets blackening at 115° to 120°.

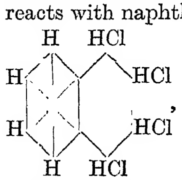
2 : 6-NAPHTHAQUINONE forms odourless, reddish yellow crystals turning grey at 135°, and is a more energetic oxidising agent than the preceding isomerides.

HYDROXYNAPHTHAQUINONE (O : O : OH = 1 : 4 : 2) is known, and its 1 : 4 : 5-isomeride is *juglone*, found in the green outer shell of the walnut and readily oxidising to a blackish-brown compound.

The following compounds are also known: Oxy- and Dioxy-naphthaquinones (*naphthazarin black*); α- and β-Methylnaphthalenes, $C_{10}H_7 \cdot CH_3$; Naphthoic acids, $C_{10}H_7 \cdot CO_2H$; Hydroxynaphthoic Acids, $C_{10}H_6(OH)(CO_2H)$; Naphthalic Acid, $C_{10}H_6(CO_2H)_2$; Dinaphthyl, $C_{10}H_7 \cdot C_{10}H_7$; Acenaphthene, $C_{10}H_6\left\langle\begin{matrix} CH_2 \\ | \\ CH_2 \end{matrix}\right.$, in which the unions with the ethylene group are in the a_1- and a_4-positions (found in tar, colourless, melting at 85°, boiling at 277°, and giving naphthalic acid on oxidation).

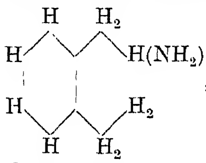
ADDITIVE PRODUCTS OF NAPHTHALENE

Naphthalene gives additive products more readily than benzene does, those containing four atoms of chlorine or hydrogen being well known. It has been shown that this addition occurs in only one of the nuclei, and similar behaviour is shown on oxidation. Chlorine reacts with naphthalene at the ordinary temperature and forms naphthalene tetrachloride,

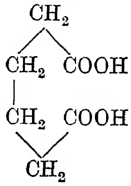


, which forms colourless crystals melting at 181° and gives phthalic acid on oxidation, and dichloronaphthalene, $C_{10}H_6Cl_2$, when treated with alcoholic potash.

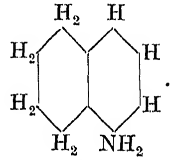
When β-naphthylamine is reduced (Na + amyl alcohol), four hydrogen atoms are added to the nucleus containing the amino-group, giving tetrahydronaphthylamine,



, which behaves exactly like an aliphatic amine and does not form diazo-compounds; it is oxidised by permanganate, giving *o*-carboxyhydrocinnamic acid, $C_6H_4\left\langle\begin{matrix} CH_2 \cdot CH_2 \cdot CO_2H \\ CO_2H \end{matrix}\right.$. α-Naphthylamine also gives a tetrahydro-derivative, which behaves, however, as an aromatic amine and can be diazotised; on oxidation it gives adipic acid,



, which shows that the four hydrogen atoms are added to the benzene nucleus which does not contain the amino-group:

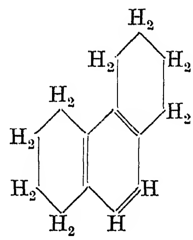


HYDRONAPHTHALENES. Dihydro- and tetrahydro-naphthalenes occur in tar, especially in that obtained from coal by direct extraction with solvents (*e.g.*, liquid SO_2) or from vacuum tar (*see* Vol. I., p. 442). Bamberger and Kitschelt (1890) hydrogenated

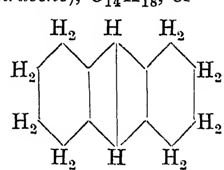
naphthalene with sodium and amyl alcohol and Sabatier and Senderens (1904–1910) with hydrogen in presence of finely divided nickel. Schroeter (1915) obtained tetrahydronaphthalene by heating pure fused naphthalene in presence of finely divided nickel with hydrogen under pressure (Ger. Pat. 324,861 and 324,862, 1915) and from naphthalene vapour and hydrogen at the ordinary pressure with the aid of various catalysts (Ger. Pat. 301,275, 1917); the naphthalene is completely purified beforehand by treating it with a readily fusible metal or with kieselguhr or animal charcoal.

The tetrahydronaphthalene obtained from the crude product by distillation in a vacuum forms an oil stable in the air, sp. gr. about 0·974, b.-pt. 206°, m.-pt. below − 20°. Its commercial name is *tetraline*, and since 1917 it has been used in various industries, *e.g.*, as a solvent for rubber, celluloid and cellon, which renders it possible to prepare softer photographic films and to obtain substitutes for backelite, gallalith, and liquid and coloured lacs (Ditmar, 1921).

In 1917 Schroeter and almost simultaneously Kantorowicz found that viscous, oily substances are formed when tetraline is heated with a little aluminium chloride. Schroeter and van Hulle (1918–1920) showed that these oils consist principally of *octahydrophenanthrene* (*octanthrene*), $C_{14}H_{18}$, or

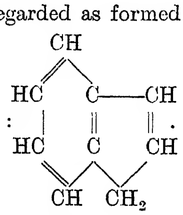


and of *octahydroanthracene* (*octhracene*), $C_{14}H_{18}$, or

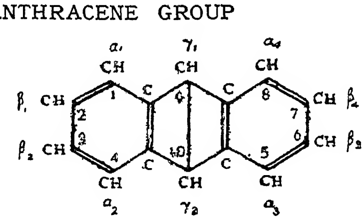


These are accompanied by a little benzene, $\beta\beta$-ditetralyl, etc.

Like those obtained similarly from petroleum hydrocarbons, such viscous products appear to have practical applications as lubricating oils, as oils for internal combustion engines, etc., and disclose new methods for utilising the large amounts of naphthalene produced.

INDENE, C_9H_8, may be regarded as formed by the condensation of a benzene group with a pentamethylene group: . It is a yellow oil boiling at 180°, and is found in coal-tar and in crude pseudocumene; it has an odour of naphthalene and gives phthalic acid on oxidation and Indrene, C_9H_{10}, on reduction.

6. ANTHRACENE GROUP

ANTHRACENE, $C_{14}H_{10}$, or  is found in coal-tar to the extent of 0·25 to 0·45 per cent. The crude anthracene oil which

passes over at a high temperature (above 270°) in the distillation of tar is subjected to a further rectification which yields a 50 per cent. anthracene. This is purified by distillation from iron retorts with potassium carbonate, which holds back the large amount of **Carbazole**, $\begin{matrix} C_6H_4 \\ | \\ C_6H_4 \end{matrix}\!\!>NH$, as the non-volatile potassium compound, $\begin{matrix} C_6H_4 \\ | \\ C_6H_4 \end{matrix}\!\!>NK$. The distillate then contains only anthracene and phenanthrene, the latter being removed by dissolving it in carbon disulphide or a mixture of this solvent with concentrated sulphuric acid (Ger. Pat. 164,508 and Fr. Pat. 349,337). The residual anthracene is purified by crystallisation from crude benzene (*see* Treatment of Tar described on pp. 630 *et seq.*), and by sublimation with superheated steam.

The proposal has also been made to purify crude anthracene (containing, say, 46 per cent. of anthracene and 13 per cent. of carbazole) with hot naphtha and sulphuric acid, which convert all the basic substances into salts and dissolve them, the anthracene being afterwards separated by decantation. Evaporation of the naphtha gives anthracene of about 84 per cent. strength, and this gives a product of 95 per cent. purity on crystallisation from benzene. In place of sulphuric acid use may be made of aqueous caustic potash solution, the distillation being carried out at 145° until water no longer passes over; the residual naphtha solution is decanted from the carbazole salt and cooled to deposit the pure anthracene (Kinzelberger, Eng. Pat. 144,648, 1920).

It forms shining, colourless scales with a blue fluorescence, and melts at 216·5° and boils at 351°; it dissolves slightly in ether or alcohol, but is readily soluble in hot benzene. Its calorific power is 9541 cals. At 100° it begins to sublime, its vapour pressure in mm. of mercury being:

100°	150°	192°	245°	265°
0·04	1·07	18·2	88·5	145·7

Sunlight gradually converts it into the polymeric *para*-**Anthracene** $(C_{14}H_{10})_2$. With picric acid it forms a molecular condensation product, $C_{14}H_{10}$, $C_6H_2(NO_2)_3OH$, melting at 138°. By reducing agents, anthracene is transformed into **Hydroanthracene**, $C_6H_4{<}{\begin{matrix}CH_2\\CH_2\end{matrix}}{>}C_6H_4$, which melts at 107° and is readily soluble in alcohol.

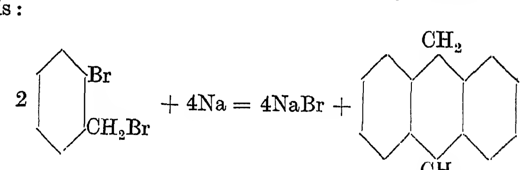
Its constitution is deduced from its various syntheses. Anschütz obtained it from tetrabromoethane and benzene in presence of $AlCl_3$:

$$2C_6H_6 + \begin{matrix} CHBr_2 \\ | \\ CHBr_2 \end{matrix} = 4HBr + C_6H_4{<}\begin{matrix} CH \\ | \\ CH \end{matrix}{>}C_6H_4.$$

It is formed also when *o*-tolyl phenyl ketone is heated with zinc dust:

$$C_6H_4{<}\begin{matrix} CH_3 \\ \\ CO \end{matrix}{\diagup}C_6H_5 = H_2O + C_6H_4{<}\begin{matrix} CH \\ | \\ CH \end{matrix}{>}C_6H_4;$$

this synthesis establishes the ortho-position of the connections between the two nuclei and also the presence of the CH · CH group. Confirmatory evidence is obtained from the following synthesis:



o-Bromobenzyl bromide

Dihydroanthracene

which, on oxidation, loses 2H and gives anthracene.

Phthalic anhydride, when heated with benzene and $AlCl_3$, gives *o*-benzoylbenzoic acid, m which PCl_5 eliminates water with formation of anthraquinone, the latter giving thracene when reduced with zinc dust in the hot:

$$H_6 + C_6H_4\left\langle\begin{matrix}CO\\ \\CO\end{matrix}\right\rangle O = C_6H_4\left\langle\begin{matrix}CO\cdot C_6H_5\\ \\COOH\end{matrix}\right. \rightarrow H_2O + C_6H_4\left\langle\begin{matrix}CO\\ \\CO\end{matrix}\right\rangle C_6H_4 \rightarrow \text{anthracene.}$$

Centric linkings do not seem to be present in the nuclei of anthracene, which readily mbines with ozone (E. Molinari, 1907), this property being characteristic of olefine double kings (*see* p. 107).

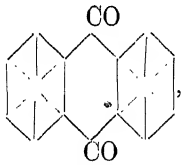
It is used in the manufacture of anthraquinone and alizarin.

Crude anthracene oil (green oil) was sold before the war at 11*s.* to 12*s.* 6*d.* per quintal, ıde 20 per cent. anthracene at 1*s.* 6*d.* per kilo, and the purified product at 6*s.* to 8*s.* r kilo.

OCTAHYDROANTHRACENE, $C_{14}H_{18}$ (*see* p. 731).

SUBSTITUTION PRODUCTS OF ANTHRACENE

The possible isomerides are here very numerous, but only few of them have t been prepared. Three monosubstituted isomerides are possible, as is seen ɔm the constitutional formula (*see above*). The constitution of the isomerides ascertained from a study of the oxidation products and of the methods of nthesis. When the substituents are in the γ_1 or γ_2 position, oxidation gives thraquinone.[1]

ANTHRAQUINONE, $C_{14}H_8O_2$, or , is obtained very easily · oxidising anthracene with dichromate and dilute sulphuric acid in the t, or, better, with nitric acid, which does not give nitro-derivatives. It n also be obtained from phthalic anhydride and benzene in presence of $AlCl_3$ *e above*) or by electrolysing anthracene in 20 per cent. sulphuric acid in presence cerium, chromium, or manganese salts (Ger. Pat. 152,063, and Perkin, 1904).

[1] Of the many **Derivatives of Anthracene**, the following may be mentioned: *anthracene-boxylic acids* (α, β, and γ); *chlorobromoanthracenes*, which contain the halogens in the ositions, as they form anthraquinone on oxidation; *nitro-* and *dinitro-anthracenes* (γ); *nthramine*, $C_{14}H_9\cdot NH_2$, obtained from β-anthrol and NH_3; *anthrols* (α and β), $I_4\left\langle\begin{matrix}CH\\|\\CH\end{matrix}\right\rangle C_6H_3\cdot OH$; *anthrone*, $C_6H_4\left\langle\begin{matrix}CH_2\\ \\CO\end{matrix}\right\rangle C_6H_4$ and its tautomeride (*see* pp. 18, 394); *nthranol*, $C_6H_4\left\langle\begin{matrix}CH—\\|\\C(OH)\end{matrix}\right\rangle C_6H_4$; *γ-hydroanthranol*, $C_6H_4\left\langle\begin{matrix}—CH_2—\\ \\CH(OH)\end{matrix}\right\rangle C_6H_4$; the *anthrahydro-nones*, $C_6H_4\left\langle\begin{matrix}C(OH)\\|\\C(OH)\end{matrix}\right\rangle C_6H_4$ (three isomerides: *chrysazol*, *rufol*, and *flavol*); *anthracene-phonic* and *disulphonic acids*; *anthraquinonesulphonic acids*; *hydroxyanthraquinones*, $H_7O_2\cdot OH$; *quinizarin* ($\alpha_1:\alpha_2$-dihydroxyanthraquinone); *purpuroxanthin* ($\alpha_1:\beta_2$-dihydroxy-hraquinone); $C_6H_4(CO_2)\cdot C_6H(OH)_3$ ($\alpha:\beta:\alpha_1$) is *purpurin* (the isomeric *flavopurpurin*, *hrapurpurin*, *anthragallol*, etc., are also known); $OH\cdot C_6H_3\cdot CO_2\cdot C_6H_3\cdot OH$ (*anthraflavinic* and *anthraflavinic acids*, with which correspond *anthrarufin*, *chrysazin*, etc.); *tetrahydroxyanthra-nones* (*rufiopin*, *anthrachrysone*, *quinalizarin*); *hexahydroxyanthraquinones* (*rufigallic acid*, etc.); *hyl-* and *dimethyl-anthracenes*, $C_{14}H_9\cdot CH_3$ and $C_{14}H_8(CH_3)_2$; *phenylanthracene*, $C_{14}H_9\cdot C_6H_5$; *ylanthrahydrides*, $C_6H_4\left\langle\begin{matrix}CH_2\\ \\CHR\end{matrix}\right\rangle C_6H_4$; *phenylanthranol* (*phthalidine*), $C_6H_4\left\langle\begin{matrix}C(C_6H_5)\\|\\C(OH)\end{matrix}\right\rangle C_6H_4$; *nylhydroxyanthranol* (*phthalideine*), $C_6H_4\left\langle\begin{matrix}C(C_6H_5)(OH)\\ \\—CO—\end{matrix}\right\rangle C_6H_4$; *anthracenecarboxylic acid* β, γ), $C_{14}H_9\cdot CO_2H$; *alkylhydroanthranols*, $C_6H_4\left\langle\begin{matrix}—CH_2—\\ \\CR(OH)\end{matrix}\right\rangle C_6H_4$, etc.

It can be purified by crystallisation from nitrobenzene or aniline, which dissolve it in the hot but not in the cold. Kinzelberger (Eng. Pat. 143,885, 1920) purifies it by heating and shaking it with chlorobenzene or solvent naphtha in presence of aqueous alkali (or with concentrated sulphuric acid), the anthraquinone solution being decanted off and the solvent removed by distillation. It gives two isomeric monosubstituted derivatives.

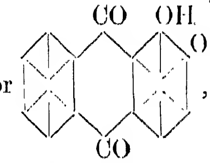
It forms yellowish needles melting at 274° and boiling above 360°, and it dissolves in concentrated sulphuric acid, but is precipitated unchanged on dilution. It is very stable, is not easily oxidised and has the character of a diketone rather than of a quinone. It is not readily reduced, is only slightly volatile and has no pungent odour. That the two lateral benzene nuclei have centric linkings and not olefinic double bonds is shown by the fact that, unlike anthracene (*see above*), anthraquinone does not fix ozone.

When fused with potash, it gives benzoic acid and, when heated with zinc dust and NaOH, **Hydroxyanthranol**, $C_6H_4 < \frac{CH(OH)}{CO} > C_6H_4$, which has a blood-red colour in alkaline solution and is oxidised to anthraquinone in the air. Reduction of anthraquinone with Sn and HCl gives **Anthranol**, $C_6H_4 < \begin{matrix} C(OH) \\ | \\ C(OH) \end{matrix} > C_6H_4$, which is a weak phenol.

More energetic reduction, such as distillation over zinc dust, yields anthracene. The Schmidt reaction permits of the introduction of sulphonic or nitro-groups into the non-substituted or the substituted nucleus of anthraquinone derivatives, according as the reaction occurs in presence or in absence of boric acid. α- or β-Nitroderivatives can also be obtained, at will, by means of the same reaction (Ger. Pat. 163,042 of 1905), which is facilitated by the presence of mercury salts.

Commercial anthraquinone cost before the war about 6*s*. per kilo, and the sublimed chemically pure product 28*s*.

The most important derivative of anthraquinone is the 1 : 2-dihydroxy-compound or alizarin.

ALIZARIN (**Dihydroxyanthraquinone**), $C_{14}H_8O_4$, or 

, was at one time obtained exclusively from madder roots (*Rubia tinctorum*), from which **Ruberythric Acid** (a glucoside of the formula $C_{26}H_{28}O_{14}$) is extracted; this is separated into glucose and alizarin by boiling with dilute sulphuric acid. It is a very beautiful red colouring-matter and was known to the ancients. Since 1870,[1] following Graebe and Liebermann's synthesis (1869), it has been prepared only artificially in the following manner: anthracene is converted by oxidation with H_2SO_4 and $Na_2Cr_2O_7$ into crude anthraquinone.

This is then heated at 100° with concentrated sulphuric acid, which leaves the anthraquinone unaltered, while it converts the impurities into sulphonic acids soluble in water. The anthraquinone is then filtered and washed and heated at 160° with fuming sulphuric acid (containing 50 per cent. of free SO_3), which converts it largely into the monosulphonic acid. The latter is dissolved in water and filtered to separate it from unaltered anthraquinone; neutralisation of the solution with caustic soda results in the deposition of the sodium salt, which is only slightly soluble in cold water. One hundred parts of this salt are mixed with 25 parts of caustic soda and 12 to 14 parts of potassium chlorate, which facilitates the reaction; the mixture is dissolved in the smallest possible amount of water and

[1] In 1868 France produced and exported madder to the value of £1,720,000 and £1,240,000 respectively. The exportation fell to £800,000 in 1871 and to £160,000 in 1876, the production then ceasing entirely.

the liquid heated at 180° for two days in an autoclave fitted with a stirrer. The sulphonic group is thus replaced by hydroxyl (or ONa), and at the same time a second OH group is formed by the action of the chlorate :

$$\underset{\text{Sodium anthraquinone-monosulphonate}}{C_6H_4<\genfrac{}{}{0pt}{}{CO}{CO}>C_6H_3 \cdot SO_3Na} + 3NaOH + O = Na_2SO_3 + 2H_2O + C_6H_4<\genfrac{}{}{0pt}{}{CO}{CO}>C_6H_2(ONa)_2.$$

The fused mass is run into water and acidified with sulphuric acid, the colouring-matter (alizarin) being thus liberated.

According to Fr. Pat. 333,144, if fuming sulphuric acid acts on anthraquinone in presence of mercury, there is no partial formation of the *m*-sulphonic compound, the sulpho-group entering exclusively the ortho-position to the ketonic group.

Alizarin may also be prepared (Ger. Pat. 186,526) without sulphonation by treating, say, 300 kilos of a mixture of NaOH and KOH with 30 kilos of $NaClO_3$ (or Na_2O_2, BaO_2, PbO_2, etc.) dissolved in 100 litres of water, 100 kilos of anthraquinone being then added and the liquid heated at 200° in an oil-bath until the oxidising agent disappears. After this, the mass is poured into water through which air is then passed ; the alizarin is precipitated with milk of lime, the precipitate being filtered off and decomposed with HCl and the alizarin purified from anthraquinone residues by means of caustic soda. This method yields a purer product than other processes.

Alizarin has been prepared recently by passing an electric current through a mixture of anthraquinone and fused potash.

Alizarin sublimes in fine, orange-red needles, melts at 289°, and is almost insoluble in water and slightly soluble in alcohol ; owing to its phenolic groups it dissolves in alkali and also forms a diacetyl-derivative. When distilled with zinc dust it forms anthracene.

With metallic oxides it forms insoluble lakes of various colours, and on this is based its use in dyeing. With ferric oxide it gives a bluish black colour and with lime a blue lake ; the lakes of tin and aluminium are red (Turkey red).

The constitution of alizarin is shown also by its synthesis from phthalic anhydride and catechol at 150° in presence of sulphuric acid :

$$C_6H_4<\genfrac{}{}{0pt}{}{CO}{CO}>O + C_6H_4<\genfrac{}{}{0pt}{}{OH\ (1)}{OH\ (2)} = H_2O + C_6H_4<\genfrac{}{}{0pt}{}{CO}{CO}>C_6H_2<\genfrac{}{}{0pt}{}{OH}{OH}.$$

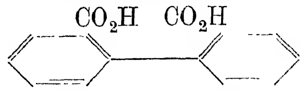
Derivatives of anthraquinone and of hydroxyanthraquinone, especially the amino-derivatives, form *colouring-matters* only when the two hydroxy-groups are in the ortho-position to one another.

PHENANTHRENE, $C_{14}H_{10}$, or $\begin{array}{l} C_6H_4 \cdot CH \\ | \qquad\ \ \| \\ C_6H_4 \cdot CH \end{array}$, is an isomeride of anthracene, with which it occurs in tar. When pure, it forms shining, colourless scales, soluble in ether, less so in alcohol (with blue fluorescence) and only slightly soluble in water ; it melts at 99° and boils at 340°. The separation of phenanthrene from anthracene is described above (*see* Anthracene). Synthetically it is obtained by condensing 1 mol. of *o*-nitrobenzaldehyde (or its higher homologues) with 1 mol. of sodium phenylacetate in presence of acetic anhydride :

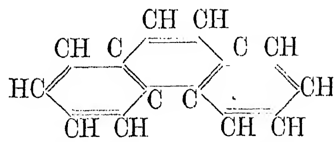
$$C_6H_5 \cdot CH_2 \cdot CO_2Na + NO_2 \cdot C_6H_4 \cdot CHO = H_2O + \underset{\text{Sodium }\alpha\text{-phenyl-}o\text{-nitrocinnamate}}{\begin{array}{r} NO_2 \cdot C_6H_4 \cdot CH \\ \| \\ C_6H_5 \cdot C \cdot CO_2Na \end{array}}$$

Reduction and diazotisation eliminate the NO_2; treatment with powdered copper then gives **β-Phenanthrenecarboxylic Acid,** $\begin{array}{l} C_6H_4\text{—}CH \\ | \qquad\quad \| \\ C_6H_4\text{—}C \cdot CO_2H \end{array}$, from which CO_2 is eliminated in the ordinary way with formation of phenanthrene.

When oxidised with chromic acid, it gives first **Phenanthraquinone**, $\begin{array}{l} C_6H_4 \cdot CO \\ | \qquad\quad | \\ C_6H_4 \cdot CO \end{array}$ (yellow crystals, m.-pt. 200°), and then **Diphenic Acid**, $C_{14}H_{10}O_4$, or



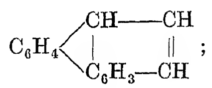
The constitution of phenanthrene is established by its syntheses and by its oxidation products. The double linking between the two methinic carbon atoms is not shown by the ordinary reaction with permanganate (Baeyer) (*see* p. 107), but is made evident by the reaction with ozone (E. Molinari, 1907; *see* p. 107). The constitutional formula of phenanthrene may be represented thus:



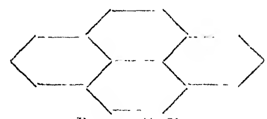
and it may, therefore, be regarded as formed by the condensation of three benzene nuclei.

OCTAHYDROPHENANTHRENE, $C_{14}H_{18}$: *see* p. 731.

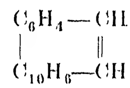
OTHER CONDENSED NUCLEI OF LESS IMPORTANCE, found in the portions of petroleum and tar distilling above 360°, are as follow:



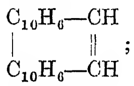
Fluoranthrene, $C_{15}H_{10}$



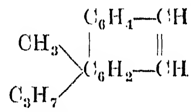
Pyrene, $C_{16}H_{10}$



Chrysene, $C_{18}H_{12}$



Picene, $C_{22}H_{14}$



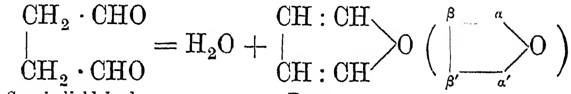
Retene, $C_{18}H_{18}$

Retene has m.-pt. 98° and b.-pt. 394°; **Chrysene**, m.-pt. 250°, b.-pt. 448°; **Picene**, m.-pt. 364°; **Fluoranthrene**, m.-pt. 110° and b.-pt. 250° (60 mm.); **Pyrene**, m.-pt. 148°, b.-pt. 260° (60 mm.).

BB. HETEROCYCLIC COMPOUNDS

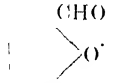
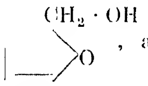
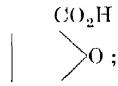
These are substances containing at least one nucleus, the atoms forming the ring being of more than one kind, *i.e.*, they are not all carbon atoms as in the *homocyclic compounds* as yet studied, one or more of these carbon atoms being replaced by nitrogen, oxygen, sulphur, etc. One of the simplest of these heterocyclic compounds is furfuran.

1. **FURFURAN** (Furan), C_4H_4O, is a colourless liquid which is insoluble in water, smells like chloroform, boils at 32°, and is found among the first products of the distillation of pine-tar. With metallic sodium it does not give hydrogen, so that the oxygen is not present as OH; nor is it in the form of carbonyl (CO), since furan does not react with phenylhydrazine or hydroxylamine. It can be converted into cœrulinic aldehyde, while, under suitable conditions, succindialdehyde loses H_2O giving furan. These reactions indicate its constitution:



Succindialdehyde Furan

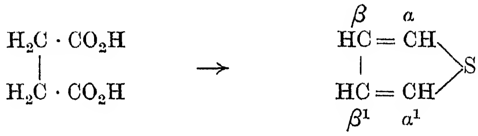
A shaving of pinewood moistened with HCl gives a green coloration with furan. The latter reacts with HCl, forming a white mass.

FURFURAL (*α*-**Furol, Furfuraldehyde**), $C_5H_4O_2$, is obtained readily and abundantly by the action of sulphuric acid on pentoses, pentosans, and woody substances (*see* p. 527); it is found in fusel oil and in clove oil. It is a colourless oil of aromatic odour, turning brown in the air and boiling at 162°; it is soluble in alcohol and, to a less extent, in water. Its aldehydic properties justify the constitution . With alcoholic potash it gives a corresponding **Furfuryl alcohol,** , and **Pyromucic acid,** ; the latter melts at 132°, sublimes readily, dissolves in hot water, decolorises alkaline permanganate and combines with 4 atoms of bromine, the presence of two true olefinic double linkings being thus confirmed. If heated in a sealed tube at 275° it gives furfuran and CO_2. With aniline and HCl, or with aniline acetate paper, it gives a characteristic intense red coloration (*see* p. 528).

2. **THIOPHEN,** C_4H_4S, occurs in tar and always accompanies benzene, on account of their similarity in boiling-point (84°) and other properties. For the preparation of benzene free from thiophen, *see* pp. 630, 633.

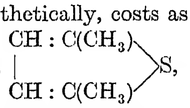
Thiophen is produced on a large scale, but in small yield, by passing acetylene or ethylene through boiling sulphur, or by passing illuminating gas over red-hot pyrites. W. Steinkopf (1911) obtains an increased yield by passing a current of acetylene over pyrites contained in a revolving iron drum and heated to 300° in a furnace, the exhausted pyrites being continually discharged and fresh pyrites introduced. The condensed liquid product contains 40 per cent. of thiophen, which can be extracted by fractional distillation.

One of the syntheses of thiophen consists in the distillation of succinic acid in presence of phosphorus sulphide, hydrogen and hydrogen sulphide being evolved; this synthesis confirms the constitution:


(Thiophen).

Thiophen is a colourless and almost odourless, refractive liquid, boiling at 84°, and having the sp. gr. 1·062 at 23°. The presence of the double linkings is confirmed by the quantitative addition of ozone.

Pure thiophen, prepared synthetically, costs as much as £18 per kilo.

Dimethylthiophen (*thioxene*), , is obtained by the interaction of the enolic form of acetonylacetone and phosphorus pentasulphide, and 1 : 4-diketones in general yield higher homologues of thiophen, which, when oxidised, give carboxyl groups in place of the side-chains.

Thiophen compounds, such as halogen and nitro-derivatives, sulphonic acids, etc., behave very similarly to those of benzene.

With isatin and concentrated sulphuric acid, thiophen gives a blue coloration (*indophenin*, $C_{12}H_7 \cdot NOS$).

3. **PYRROLE,** C_4H_5N, is found in small quantity in tar and in larger quantity in Dippel animal oil (*bone oil*), especially in the fraction distilling at about 130°, which is freed from pyridine bases by saponifying with soda and washing with dilute sulphuric acid. It is purified by converting into the potassium derivative, C_4H_4NK (by the action of potassium), which is washed with ether, in which it is insoluble, and then treated with water, the pyrrole being thus liberated.

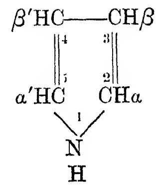
After fractional distillation, it is obtained as a light, colourless oil, boiling at 131°, and possessing a faint odour of chloroform. It readily turns brown and polymerises under the action of light. With isatin and sulphuric acid it gives the blue indophenin reaction (*see above*).

A *reaction characteristic of the pyrroles* is the red coloration they give with a pine shaving moistened with HCl.

The hydrogen of the iminic group is replaceable by metals, acetyl, and alkyl groups.

Pyrrole now forms the basis of a number of important compounds, which are obtained by various syntheses investigated by Ciamician and his collaborators during the past quarter of a century.

The constitutional formula of pyrrole is as follows:



this being deduced from a number of reactions and syntheses, *e.g.*, the formation of pyrrole by the action of ammonia on γ-diketones or on succinic aldehyde, with intermediate formation of diammonaldehyde:

$$\begin{array}{l} CH_2 \cdot CHO \\ | \\ CH_2 \cdot CHO \end{array} + NH_3 = 2H_2O + \begin{array}{l} CH : CH \\ | \\ CH : CH \end{array} \!\!> NH.$$

This pyridine nucleus occurs frequently in nature, in combination with other groups in alkaloids (nicotine, etc.), in the colouring-matter of the blood and of chlorophyll, etc.

When boiled with hydroxylamine, pyrrole gives succindialdoxime, $\begin{array}{l} CH_2 \cdot CH : N \cdot OH \\ | \\ CH_2 \cdot CH : N \cdot OH \end{array}$, which, with nitrous acid, gives succinic aldehyde, $\begin{array}{l} CH_2 \cdot CHO \\ | \\ CH_2 \cdot CHO \end{array}$.

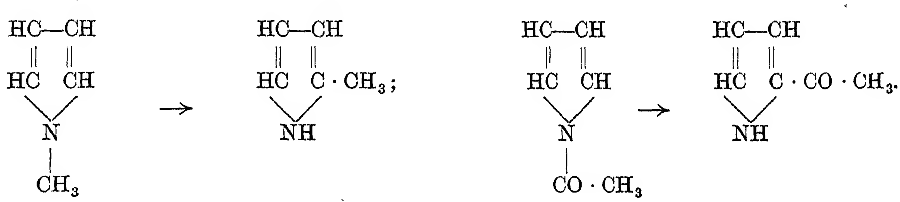
Pyrrole is formed by the distillation of succinimide, $\begin{array}{l} CH_2 \cdot CO \\ | \\ CH_2 \cdot CO \end{array} \!\!> NH$, with sodium or zinc dust, while the oxidation of pyrrole with chromic acid gives maleimide, $\begin{array}{l} CH \cdot CO \\ \| \\ CH \cdot CO \end{array} \!\!> NH$.

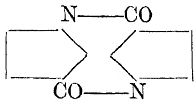
Pyrrole is changed by acids; with HCl in the hot, it polymerises and condenses to a red mass (*pyrrole red*). It has a faint basic character, but gives a hydrochloride, $(C_4H_5N)_3$, HCl, only in ethereal solution.

With the halogens it gives not additive products but only, like benzene, substituted derivatives. **Tetraiodopyrrole** (*iodol*) is obtained from pyrrole by the action of an alcoholic, alkaline solution of iodine; it is an efficient antiseptic and is used instead of iodoform, being without the unpleasant odour of the latter. It melts at 190°, and is colourless when freshly prepared, but it gradually turns brown and deposits iodine.

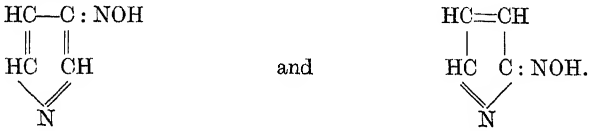
With nitric and sulphuric acids, pyrrole resinifies; the nitro-derivatives, which contain the *isonitro*-group, NOOH, are prepared indirectly (*e.g.*, with alkyl nitrate).

Pyrrole is analogous in many of its properties to the substituted phenols and anilines; thus, a methyl- or acetyl-group united to the nitrogen (N-derivatives) is displaced, on heating, to a carbon atom (C-derivatives):

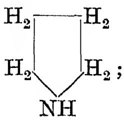


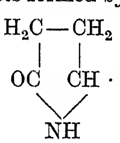
Potassium pyrrolate, C_4H_4NK, and CO_2 give pyrrolecarboxylic acid, $C_4H_3(CO_2H) \cdot NH$ (m.-pt. 102°); this loses CO_2 and gives pyrrole again when heated, while it loses water and forms a dimolecular anhydride, **Pyrocoll**, , when treated with acetic anhydride.

Like the substituted phenols, the C-alkylpyrroles give pyrrolecarboxylic acids by simple fusion with potash. In analogy with the formation of nitrosophenols from phenols, pyrrole, with ethyl nitrite in presence of sodium alkoxide, forms **Nitrosopyrrole**, which exists in tautomeric modifications:

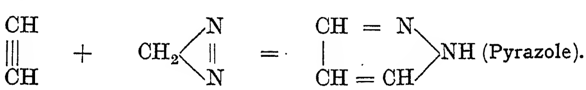


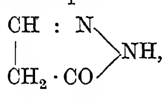
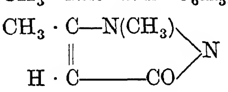
By means of chloroform and sodium alkoxide, another atom of carbon is introduced into the nucleus, a pyridine derivative being formed.

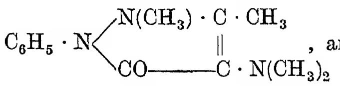
Hydrogenated derivatives of pyrrole are formed more easily than those of benzene, and, like the latter, do not show purely aromatic properties. When pyrrole is reduced by means of zinc and hot acetic or cold hydrochloric acid, it yields **Dihydropyrrole** (or *pyrroline*, m.-pt. 91°), which, with HI and P, gives **Tetrahydropyrrole** (or *pyrrolidine*, b.-pt. 87°), ; the latter, together with N-methylpyrroline, are the simplest cyclic alkaloids known and are found in tobacco. Pyrrolidine is found in carrot seeds and a C-methylpyrroline in pepper.

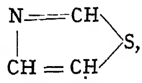
When proteins are decomposed by means of trypsin or hydrochloric acid, the amino-acids formed are accompanied by lævo-rotatory **α-Pyrrolidinecarboxylic Acid.** Among the products formed by the degradation of egg albumin by baryta is **α′-pyrrolidone-α-carboxylic acid,** , which is also known as *pyroglutamic acid*; it melts at 183°, has a neutral reaction and, when heated, loses CO_2 and H_2O, forming pyrrole.

PYRAZOLE, $C_3H_4N_2$, is a heterocyclic compound with two nitrogen atoms in the ortho-positions. It can, indeed, be obtained by the condensation of 1 mol. of diazomethane with 1 mol. of acetylene:

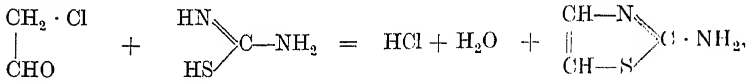


It is very stable, melts at 70°, is a feeble base, and has a neutral reaction in water. The α′β′-dihydro-compound is known as **Pyrazoline,** $C_3H_6N_2$, and the α′-keto-derivative of this, , as **Pyrazolone.** Condensation of methylphenylhydrazine, $CH_3 \cdot NH \cdot NH \cdot C_6H_5$, with ethyl acetoacetate yields **Dimethylphenylpyrazolone**, , which bears the name *antipyrine* and is used medicinally owing to its marked antipyretic action on the animal organism; it melts at 113°, dissolves in water and in alcohol, and gives a greenish blue coloration with nitrous acid and a red coloration with ferric chloride.

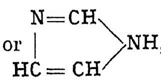
PYRAMIDONE is dimethylaminoantipyrine or phenyldimethylaminopyrazolone, , and is prepared by reducing isonitrosoantipyrine, with subsequent alkylation (Meister, Lucius und Brüning, Ger. Pat. 71,261, 1891). It forms a white crystalline powder, m.-pt. 108°, has a somewhat bitter taste, and dissolves readily in alcohol and in 18 parts of cold water. It is used as an antipyretic, the dose being 0·3 grm.

THIAZOLE, C_3H_3NS, or , may be regarded as thiophen with one CH group replaced by N. It shows analogies with the pyridine bases. Just as benzene may be obtained from aniline, thiazole may be obtained from aminothiazole (*see below*).

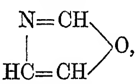
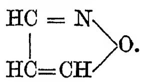
AMINOTHIAZOLE, $C_3H_2NS \cdot NH_2$, is obtained by the action of monochloracetaldehyde on pseudo-thiourea :

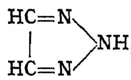


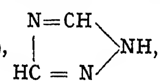
and is a base analogous to aniline.

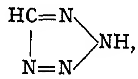
IMINAZOLE or Glyoxaline, $C_3H_4N_2$ or , melting at 92°, is a strong base with a fishy odour, and is isomeric with pyrazole (*see above*) ; it is obtained by the action of ammonia on glyoxal in presence of a little formaldehyde. Alloxan (*see* p. 435) may be regarded as a derivative of iminazole.

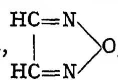
LYSIDINE, Methyldihydroiminazole or Ethenylethylenediamine, $C_3H_3(CH_3)N_2H_2$, is administered as a solvent for uric acid.

OXAZOLE, C_3H_3NO, or , is also termed Furazole, owing to its analogy with furfuran (*see above*). Its phenyl derivatives are known, as also are those of Isooxazole, .

OSOTRIAZOLE, , is faintly acid and also faintly basic in character. It melts at 22°, boils at 204°, and is soluble in water.

TRIAZOLE (or Pyrrodiazole), , melts at 121°, and is extremely soluble in water.

TETRAZOLE, , is a weak acid which forms explosive salts ; it melts at 155° and is soluble in water.

AZOXAZOLE, , is also termed Furazan.

4. PYRIDINE AND ITS DERIVATIVES

Pyridine is a heterocyclic nucleus containing 5 carbon atoms and 1 of nitrogen. It resembles benzene in its behaviour, but it is more stable or more indifferent towards sulphuric, nitric, and chromic acids, permanganate, etc. Oxidation of the homologues with side-chains gives pyridinecarboxylic acids, and the latter, when distilled with lime, give pyridine.

Its hydro-derivatives are readily formed in a similar manner to hydrobenzenes.

Halogen derivatives are obtained more easily by the action of PCl_5 or $SbCl_5$ at a high temperature than by the action of the halogens themselves.

Oxidising agents attack only the side-chains and not the pyridine nucleus. With sulphuric acid, a pyridinesulphonic acid is obtained, and this gives a hydroxyl-derivative of pyridine on fusion with potash, or a nitrile when treated with KCN. There is hence a marked analogy to benzene, although direct nitration of pyridine is not possible unless phenolic or aminic groups are present.

Pyridine and its derivatives are decidedly basic in character (tertiary bases) and form soluble salts with hydrochloric or sulphuric acid and insoluble ones with chromic acid; the double salts with platinum and gold chlorides are slightly soluble. Like tertiary bases, they combine with methyl iodide to form quaternary bases.

From the complex alkaloidal groupings, pyridine compounds are often obtained either by distillation with caustic potash or merely by energetic oxidation.

Coal-tar and Dippel animal oil contain various pyridine compounds which are separated after conversion into salts.

General Methods of Formation. (*a*) The oxidation of quinoline (*see later*) yields first quinolinic acid (pyridinedicarboxylic acid), $C_5H_3N(CO_2H)_2$, which then loses CO_2, giving pyridine. β-Methylpyridine is obtained by distilling acraldehyde-ammonia; this explains the presence of pyridine products in Dippel oil, acroleïn and ammonia being formed in the dry distillation of non-defatted bones.

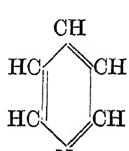
An important synthesis is the general one of Hantzsch by which **ethyl dihydrocollidinedicarboxylate,** for example, is obtained by heating aldehyde-ammonia with ethyl acetoacetate; other pyridine compounds are obtained from different aldehyde-ammonias and β-ketonic acids:

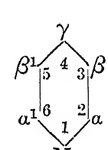
$$2CH_3 \cdot CO \cdot CH_2 \cdot CO_2C_2H_5 + CH_3 \cdot CHO + NH_3 = \\ C_5N(CH_3)_3H_2(CO_2C_2H_5)_2 + 3H_2O.$$

From the ester thus formed the hydrogen of the NH and CH is eliminated by means of nitrous acid, and the resulting collidinedicarboxylic acid, when treated with potash and distilled with lime, loses the two carboxyls and gives collidine (trimethylpyridine); oxidation of the latter gives pyridinecarboxylic acid, and elimination of carboxyl from this in the ordinary way forms pyridine.

When ethylidene chloride is heated with alcoholic ammonia, it yields **Aldehydine,** $C_8H_{11} \cdot N$.

The *constitution of pyridine* corresponds with that of benzene in which one methinic group, CH, has been replaced by a nitrogen atom. Körner in 1869 proposed the following constitutional formula, which still agrees well with all the general properties of the pyridine compounds:





When pyridine is reduced with alcohol and sodium, it fixes six atoms of hydrogen, giving piperidine or hexahydropyridine, the constitution of which is shown by its synthesis when pentamethylenediamine hydrochloride is rapidly heated:

$$CH_2\left\langle\begin{matrix} CH_2 \cdot CH_2 \cdot NH_2 \\ CH_2 \quad CH_2 \cdot NH_2 \end{matrix}\right. = NH_3 + CH_2\left\langle\begin{matrix} CH_2 \cdot CH_2 \\ CH_2 \cdot CH_2 \end{matrix}\right\rangle NH.$$

When piperidine is heated with sulphuric acid it gives pyridine, and the latter, when strongly heated with hydriodic acid, gives normal pentane. The constitution of pyridine is confirmed by the fact that the isomeric substitution products correspond exactly in number with those derivable theoretically from Körner's formula. There are, indeed, three monosubstituted isomerides (α, β, and γ), and six disubstituted isomerides: $\alpha\alpha'$, $\alpha\beta$, $\alpha\beta'$, $\beta\gamma$, $\beta\beta'$, and $\alpha\gamma$.

The position of a substituent group is determined by converting it into a carboxyl group with formation of the corresponding acid of known constitution (*see later*). Thus, picolinic acid has the carboxyl in the α-position, nicotinic acid in the β-, and isonicotinic acid in the γ-position.

PYRIDINE, C_5H_5N, is a colourless liquid, boiling at 115° and having the sp. gr. 1·0033 at 0°. It dissolves in water in all proportions and has a slight alkaline reaction (not sensitive to phenolphthalein, slightly to litmus, and more so to methyl orange).

It has an unpleasant odour and is hence used to denature alcohol (*see* p. 177).

It forms a slightly soluble ferrocyanide, by means of which it can be purified. It forms pyridineammonium iodides, *e.g.*, C_5H_5N,CH_3I, which with KOH in the hot gives **dihydromethylpyridine**, $C_5H_4H_2 \cdot NCH_3$, with a characteristic pungent odour.

Metallic sodium polymerises pyridine, forming **dipyridine**, $C_{10}H_{10}N_2$ (b.-pt. 290°), and **γ-dipyridyl**, $C_{10}H_8N_2$ or $NC_5H_4 \cdot C_5H_4N$ (m.-pt. 114°). With sulphuric acid it gives **β-pyridinesulphonic acid**, $NC_5H_4 \cdot SO_3H$.

Pyridine is administered in cases of asthma and has been suggested as a means of purifying synthetic indigo.

Mixed pyridine bases for denaturing cost before the war about 1*s*. 2*d*. per kilo and pure pyridine 8*s*.

Of the homologues of pyridine, the following may be mentioned:

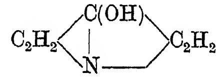
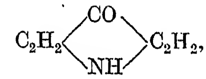
PICOLINE (**Methylpyridine**), $NC_5H_4 \cdot CH_3$, exists as three isomeric liquids similar to pyridine and of disagreeable odour; their boiling-points are: α, 129°; β, 142°; γ, 144°. Besides by general synthetical methods (*see above*), β-picoline is formed by heating strychnine with lime. α-Methylpyridine condenses with aldehydes by means of the methyl group, giving *alkines*: $NC_5H_4 \cdot CH_3 + CH_3 \cdot CHO = NC_5H_4 \cdot CH_2 \cdot CH(OH) \cdot CH_3$. This *$\alpha$-picolylalkine* gives up a molecule of water yielding a pyridine derivative with an unsaturated side-chain, *e.g.*, α-allylpyridine, $NC_5H_4 \cdot CH : CH \cdot CH_3$.

These reactions proceed in one stage if zinc chloride is present with the aldehyde.

LUTIDINES (**Dimethylpyridines**), $NC_5H_3(CH_3)_2$; three isomerides are known, with the boiling-points: $\alpha\alpha'$, 143°; $\beta\beta'$, 170°; $\alpha\gamma$, 157°.

COLLIDINES (**Trimethylpyridines**), $NC_5H_2(CH_3)_3$, are isomeric with propylpyridine. α-Allylpyridine (*see above*) fixes hydrogen (alcohol and sodium), giving the alkaloid **CONIINE** (inactive racemic), which is **α-propylpiperidine**; fractional crystallisation of the tartrate separates the lævo- from the dextro-form, the latter being identical with natural coniine (the poison of hemlock), boiling at 167°. The asymmetric carbon atom causing the activity is the α- one united with the propyl group.

PYRIDONES or **HYDROXYPYRIDINES**, $NC_5H_4 \cdot OH$. The three isomerides are known, their boiling-points being: α, 107°; β, 124°; and γ, 148°. They are obtained by heating the corresponding hydroxypyridinecarboxylic acids with lime. They are phenolic in character and give red or yellow colorations with ferric chloride. α-Hydroxypyridine forms two series of derivatives corresponding with the two tautomeric formulæ:

 and 

the former giving, for instance, a methoxypyridine and the latter a **methylpyridone**.

PYRIDINEMONOCARBOXYLIC ACIDS, $NC_5H_4 \cdot CO_2H$. The three isomerides are as follow: α or picolinic acid, m.-pt. 135°; β or nicotinic or nicotic acid, m.-pt. 231°; γ or isonicotinic acid, m.-pt. 309°.

They are formed by oxidation of pyridine derivatives with a side-chain or by elimination of one carboxyl from the pyridinedicarboxylic acids, that nearer to the nitrogen being the

more easily eliminated. Nicotinic acid is obtained on oxidation of nicotine. When boiled with sodium amalgam in a highly alkaline solution, these acids lose nitrogen as NH_3 and give saturated, open-chain, dibasic hydroxy-acids.

When the carboxyl is in the α-position (with the dicarboxylic acids also), an orange coloration is given with $FeSO_4$.

As they are both acid and basic in character, they exhibit analogies with glycocoll (*see* p. 423).

The **PYRIDINEDICARBOXYLIC ACIDS**, $NC_5H_3(CO_2H)_2$, have the following melting-points: $\alpha\alpha'$ or dipicolinic acid, 226°; $\beta\beta'$ or dinicotinic acid, 323°; $\alpha\beta$ or quinolinic acid, 190°; $\alpha\beta'$ or isocinchomeronic acid, 236°; $\alpha\gamma$ or lutidinic acid, 235°; $\beta\gamma$ or cinchomeronic acid, 249°.

Quinolinic acid is formed by the oxidation of quinoline, its constitution being thus established, and since in the hot it loses CO_2 from the α-position, giving nicotinic acid, the constitution of the latter is also fixed.

Pyridinetricarboxylic acids (obtained by oxidising cinchonine or quinine), as well as **pentacarboxylic acids** and **hydroxypyridinecarboxylic acids**, are also known.

HYDROPYRIDINES. The **dihydropyridines** are mentioned above. The *tetrahydropyridines* and their derivatives are known also as *piperideines*, while the *hexahydropyridines* and their derivatives—included in the term *piperidines*—embrace *pipecoline*, $NC_5H_{10} \cdot CH_3$; *lupetidine*, $NC_5H_9(CH_3)_2$; *copellidine*, $NC_5H_8(CH_3)_3$, etc.

PIPERIDINE, NC_5H_{11}, is obtained by heating piperine or *piperylpiperidine*, $C_5H_{10}N \cdot C_{12}H_9O_3$ (m.-pt. 129°), which is the alkaloid contained in pepper, and is formed by the condensation of 1 mol. of *piperic* or *piperinic acid*, $C_{12}H_{10}O_4$, or

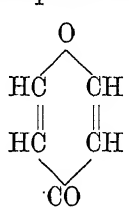
$$CH_2{<}{}^{O}_{O}{>}C_6H_3 \cdot CH : CH \cdot CH : CH \cdot CO_2H,$$

with 1 mol. of piperidine. For the constitution and syntheses of the latter, *see* p. 741.

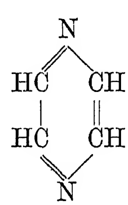
Piperidine boils at 106°, has an odour of pepper, is strongly basic, and is soluble in water or alcohol. With H_2O_2 it gives aminovaleraldehyde.

Piperidine, being a secondary base, forms with $2CH_3I$ an ammonium iodide derivative which, when distilled with silver oxide, gives an unsaturated open-chain, tertiary base; in its turn the latter, with CH_3I, Ag_2O and distillation, loses trimethylamine and forms **piperilene**, $CH_2 : CH \cdot CH_2 \cdot CH : CH_2$.

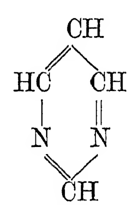
To the group of heterocyclic compounds belong the following, which are of little importance:



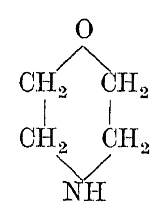
Pyrone or *pyrocomane* (m.-pt. 32°); the isomeric α-pyrone is *coumalin*



Pyrazine or *aldine* (m.-pt. 47°) is basic and with H gives *piperazine*, $C_4H_{10}N_2$



Pyrimidine or *m*-diazine (m.-pt. 22°)



Morpholine, a base, b.-pt. 129°

From these compounds may be derived *coumalinic* or *comanic acid*, $C_5H_3O_2 \cdot CO_2H$ (also formed from malic acid); **meconic acid**, $C_5HO_2(OH)(CO_2H)_2$, which can be obtained from opium and gives *pyromeconic acid* by elimination of CO_2; **chelidonic acid**, $C_5H_2O_2(CO_2H)_2$, which is found in celandine, loses CO_2 giving comanic acid and pyrone.

ALKALOIDS

These are found in various plants and have medicinal and often poisonous properties; some of them, such as caffeine, theobromine, etc., were described on pp. 437 *et seq.*, and the principal ones having basic characters (*vegetable bases*) will be considered here.

They are almost all lævo-rotatory and have an alkaline reaction and a

bitter taste. They are soluble in alcohol and to a less extent in ether, and are usually insoluble in water and in alkali; in acids they dissolve with formation of crystallisable salts. Nearly all alkaloids are precipitated from their solutions by tannin, phosphomolybdic acid, potassium mercury iodide, HgI_2, KI, or aromatic nitro-derivatives (*e.g.*, picric acid, etc.), etc.[1] From plants they are extracted with acid solutions and are then liberated with alkali and either distilled in steam or, if they are non-volatile, filtered off.

When converted into salts by means of strong acids, their specific rotatory power is not greatly influenced, since these acids are almost completely dissociated in aqueous solution; with weak acids, however, the salts are only slightly dissociated, and hence the rotatory power is different, being due to very different ions.

A. Pictet (1906) regards the alkaloids not as assimilation products of the organism, but rather as nitrogenous decomposition products of proteins, nucleins, chlorophyll, etc., which have condensed with other substances present in the plants. It is supposed that alkaloids containing the pyrrole group have their origin in protein or chlorophyll, in which such group is certainly present, while those with a pyridine grouping have a similar origin, the transformation of the pyrrole into the pyridine nucleus being possible even in the laboratory; the pyridine or quinoline group itself does not appear to exist in the proteins, chlorophyll, etc.[2]

[1] **Separation and Tests of Alkaloids.** A mixture of these is separated as follows:

I. From the neutral or acid aqueous solution, ether extracts: *digitalin*, *picrotoxin*, and *colchicine*, and from a solution of these the first and last are precipitated by tannin.

II. From the alkaline aqueous solution, ether extracts: *coniine*, *nicotine*, *brucine*, *delphinine*, *narcotine*, *veratrine*, *atropine*, *strychnine*, *aconitine*, *quinine*, *codeine*, and *physostigmine*.

III. From the alkaline aqueous solution, chloroform extracts: *cinchonine*, *caffeine*, *curarine*, *morphine*, *solanine*, and *theobromine*.

The separate alkaloids can be distinguished by the following colorimetric tests, arranged by Hager. The colours are represented shortly (as with the colouring-matters; *see later*) as follow: O = orange; B = blue; Br = brown; D = decolorised or colourless; Y = yellow; Gr = grey; Bl = black; R = red; r = rose; Gn = green; V = violet; + = intense; — = weak. The reagents most commonly used are:

(1) *Erdmann's reagent:* to 20 drops of a solution containing 10 drops of HNO_3 (sp. gr. 1·153) and 20 c.c. of water are added 40 c.c. of concentrated H_2SO_4. One cubic centimetre of this liquid is poured on to 1 to 2 grms. of the dry alkaloid and the changes observed after 15 to 30 minutes.

(2) *Fröhde's reagent:* 0·5 grm. sodium molybdate in 100 c.c. conc. H_2SO_4.

(3) *Mandelin's reagent:* 1 grm. ammonium vanadate in 200 grms. H_2SO_4 (monohydrate).

(4) *Marquis's reagent:* a solution of formalin in sulphuric acid.

(5) *Lafon's reagent:* sulphuric acid solution of ammonium selenite.

[2] **Synthesis of Alkaloids and Medicine.** Even during the most remote ages human beings sought remedies for their ailments in the principles contained in various plants and animals. Galen (A.D. 131–200) studied various medicines more rationally than had been previously done by Hippocrates (400 B.C.).

Numerous medicines proposed by Galen were used as sovereign remedies for some centuries, until indeed Paracelsus (1493–1541) gave a new direction to medicine by contesting the theory of Galen and of Avicenna and by founding *iatrochemistry*, which had such a large following in the Middle Ages, and which ultimately degenerated into the most fantastic sorcery (*see* "History of Chemistry," Vol. I., p. 14).

Modern chemistry alone could yield medicine real support, by rigorous control of the physiological and chemical actions of all the natural and artificial drugs.

In the past the curative properties of various substances were discovered by pure chance; this was the case, for instance, with antifebrin (acetanilide), which was administered to a patient in mistake for naphthalene. Nowadays, however, a rational procedure is followed, use being made either of analogy in chemical constitution between the substance under consideration and others of known action or of systematic physiological tests, first on animals and afterwards on human beings.

Until the beginning of the nineteenth century, the energies of chemists were directed to the discovery of the active and essential principles of those parts of plants successfully applied in medicine. When these were isolated in the pure state, attempts were made to establish their chemical structures and, in some cases, to effect their manufacture synthetically.

As early as 1805 Sertürner discovered and isolated *morphine*, the active principle of opium, and in 1821 Pelletier and Caventou discovered the alkaloids of cinchona bark, which were studied in 1850 by Strecker with the object of ascertaining their chemical constitution. The synthesis of these alkaloids was by no means an easy task, but in cases where they themselves have not been obtained by laboratory reactions, simple derivatives have been prepared, and these often

Alkaloid	H_2SO_4 conc.	HNO_3 sp. gr. 1·4	Erdmann's reagent	Fröhde's reagent	Mandelin's reagent	Marquis's reagent	Lafon's reagent	2 per cent. aqueous furfural
Aconitine	Y-Br; after 24 hours Br-R; after 48 hours D	Y	Y-Br; in the hot R-Br	Y-Br, then D	—	—	—	—
Atropine	D or Br	substance Br, solution D	D	D	—	—	—	—
Brucine	− r	+ R, then O	R and then Y	R, then Y; after 24 hours D	—	—	r	—
Quinine	D	D	− D	D or − Gn	—	—	—	-
Quinidine	− D	D	− D	− D	—	—	-	—
Cinchonine	D	D	D	D	—	—	-	—
Digitalin	Br then R	− Br	R-Br, then R; after 15 hours + R	+ O then + R; in 30 minutes Bl-Br; after 24 Gn-Y	—	—	- -	- -
Caffeine	D	D	D	D	—	—	—	—
Codeine	D, after 8 days B	r then Y	D then B	Gn then B or after 24 hours − Y	Gn in hot B	V	Gn	—
Cocaine	D	D	D	D	—	—	—	—
Colchicine	+ Y	V then B and Y	Y	Y and − Gn-Y	—	—	—	—
Coniine	D	D then − Y then D	D	Y	—	—	—	—
Morphine	D, in hot R then V and Gn	O then Y	− R then Br	V, then Gn, Br, after 24 hours V	—	R	Gn	R
Narcotine	− Y then O and after 24 hours r	Y then D	Y, O	Gr, then Br, Y, r	R	—	Gn-Br, in the hot R	—
Narceine	Br then Y	Y	Y then − Br	Br then Y and D	O, in the hot R	Y	B, Br	—
Nicotine	D	Y then R-V and then D	D	Y then r	—	—	—	—
Papaverine	V then B	O	V then B	V then B Y D	—	—	—	—
Physostigmine	Y then Gn	—	—	—	—	—	—	—
Piperine	R then O	O and with alkali R	− Y-Br	Y then + Br Bl	Br-Gn	R	Gn Br	Y-Gn to GnB
Solanine	O, and after 20 hours Br	D then − B	− Y	R then Br and Y	O	Br	R-Br	R then Y
Strychnine	D and with bichromate V	Y	D; with MnO_2 V then R	D	V	—	—	—
Thebaine	R then O	Y	R then O	R then O and D	R	R	—	− R then D
Theobromine	D	D	D	D	—	—	—	—
Veratrine	O then R	Y	O then R	Y then R	R	R Br	—	V, in hot B
Adrenaline	—	—	—	Y Br then Gn R	Y, Br	R Br	Gn	− Y
Berberine	Gn	+ R Br	Gn	Gn-Br	B V then V Br	Y in hot, Gn	Br Gn	—
Hydrastine	—	—	—	Gn Gr	R	—	Br	—
Picrotoxin	—	—	—	O	Y Gn	− R	—	—
Digitoxin	—	—	—	Br	Br V	r	Br V	V

exhibit similar therapeutic properties. Thus synthesis has given *codeine* (or methylmorphine) and *dionine* (ethylmorphine), which in many cases are excellent substitutes for morphine, as they are scarcely if at all poisonous. Derivatives of cocaine, such as *eucaine* (a derivative of γ-methoxy-piperidine; Ger. Pats. 90,235 and 97,672), and of quinine, such as *euquinine* (the carbethoxy-derivative of quinine, without the bitter taste of the mother-substance), have also been prepared.

Chemical investigation not only gives new products but leads to improved manufacture and consequent cheapening of the old ones. Thus, quinine, which 20 years ago cost £40 per kilo, was sold before the war in a highly pure state for 32*s*. Vast works now turn out enormous quantities of synthetic drugs, although these are administered in doses of centigrams; thus, *antipyrine*, discovered by Knorr, was consumed to the extent of hundreds of thousands of kilos in the first few years during which *influenza* made its appearance.

Modern industrial conditions have rendered possible the development of *serotherapy* (*see* p. 138), and great results are now promised by *organotherapy* or *ototherapy*. This is based on the fairly general phenomenon that in the different organs of a healthy individual substances are continually produced capable of guarding them against different affections. This principle, introduced vaguely and confusedly by Brown-Séquard in France in 1891, was in 1895 brought forward

The work of Pictet and of Ellinger has shown how these groups, occurring in the alkaloids, may be derived from the transformation of the pyrrole and indole groups. Ciamician and Ravenna (1911–1913) found that the production of

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with triumph by Baumann, who found that in many persons goitre is due to deficient secretion of iodo-products by the thyroid glands (*see* Vol. I., p. 162), and, having extracted the active iodine principle, *thyroidin*, from the thyroid of healthy sheep, that this constitutes a rapid and effective cure for goitre. For the treatment of other diseased organs, *ovarin*, *cerebrin*, *nuclein*, etc., were prepared from the corresponding organs of healthy animals.

Coal-tar derivatives have been employed for the synthesis, not only of artificial alkaloids, antipyretics, and antiseptics, but also of an important group of *anæsthetic* or *hypnotic* substances which have been of great service to medicine and especially to surgery in rendering painless the most complicated operations. At first, substances such as *ether* and *chloroform* were employed which produced *general anæsthesia* of the organism, but the use of these, especially of chloroform, was attended by much inconvenience and often by death of the patient. Sulphuric ether was recognised as an anæsthetic by Faraday as early as 1818, but it was used for the first time by the American doctor, C. W. Long, in 1842.

The anæsthetic is carried by the blood into contact with the nerve-centres which perceive pain, producing a poisoning and a paralysis which last for some time, but at the same time those centres which govern the action of the heart and of respiration are also affected, thus causing the dangers and disturbances accompanying general anæsthesia. The nervous currents start from the periphery, from the points where the surgical operation begins, and are transmitted to the brain, which transforms them into the sensation of pain, and it is precisely by the influence of the anæsthetic on the cerebral centres that pain is avoided. Anæsthesia ceases to be dangerous when the paralysis is effected on the peripheral nerve-centres at the beginning of the nervous currents, without, however, reaching the brain. In this way the ideal of *local anæsthesia* was arrived at, this being much more rational and much less dangerous, since by its means only the single organ or region of the body to be operated on is rendered insensible.

To *chloroform*, *ether*, etc., were added, in 1885, *cocaine*, which paralyses only the sensitive peripheral nerves and does not influence the motor nerves. It can now be indicated which specific atomic groupings in the molecules of *anæsthetics or hypnotics* confer on these their special properties.

Hypnotics include those of (1) the chloral hydrate group, to which belong also chloralamide (chloralformamide) and paraldehyde; (2) the tert.amyl alcohol class, $\genfrac{}{}{0pt}{}{CH_3}{CH_3}{>}C{<}\genfrac{}{}{0pt}{}{C_2H_5}{OH}$, characterised by the presence of a hydroxyl and of a carbon atom united to three alkyl groups, the action of these compounds increasing with the molecular weight; (3) the intermediate *dormiol* [tert. amylchloral, $CCl_3 \cdot CH(OH)(OC_5H_{11})$] class; (4) the urethane derivatives, including *hedonal* [methylpropylcarbinol urethane, $NH_2 \cdot CO \cdot O \cdot CH(CH_3)(C_3H_7)$]; (5) a group of compounds containing a single carbon atom united to two alkyl groups and to two sulphonic residues, *e.g.*, *trional*, $\genfrac{}{}{0pt}{}{CH_3}{C_2H_5}{>}C{<}\genfrac{}{}{0pt}{}{SO_2 \cdot C_2H_5}{SO_2 \cdot C_2H_5}$ (*methylsulphonal* or diethylsulphonemethylethylmethane); (6) a group studied by E. Fischer and consisting of urea derivatives, *e.g.*, $NH_2 \cdot CO \cdot NH \cdot CO \cdot CH(C_2H_5)_2$ (*diethylacetylurea*) or, better, *diethylmalonylurea*, $CO{<}\genfrac{}{}{0pt}{}{NH \cdot CO}{NH \cdot CO}{>}C{<}\genfrac{}{}{0pt}{}{C_2H_5}{C_2H_5}$ (diethylbarbituric acid), which bears the name of *veronal* (m.-pt. 191°; it was prepared by E. Fischer and J. Mering, patented by Messrs. Merck in 1903 and then made by Messrs. Fr. Bayer, of Elberfeld) and serves to replace chloroform, being free from the dangerous consequences of the latter (provided that it is not administered to patients with weak kidneys). Change of the alkyl groups in veronal is accompanied by change in the properties; thus, dimethylbarbituric acid has no hypnotic properties, dipropylbarbituric acid is more effective than veronal, while dibenzylbarbituric acid is without action, possibly owing to its slight solubility.

According to H. Meyer and Overton, all substances capable of dissolving fats are more or less anæsthetic, and according to Nicloux (1909) the substance of the nervous system contains an abundance of *lipoids*, *i.e.*, of compounds soluble in the same solvents as fats and hence capable of fixing the anæsthetics (they may contain nitrogen and also phosphorus). Thus the quantity of anæsthetic fixed by the organism and hence effective is directly related to the quantity of lipoids present in the various parts of the body. It is also interesting that structural isomerism produces marked change in the physiological action, *tropacocaine*, for instance, being an anæsthetic, while *benzoyltropine* acts as a mydriatic.

Of the numerous other anæsthetics, *orthoform* (methyl ester of *m*-amino-*p*-hydroxybenzoic acid), *alipine*, *holocaine*, may be mentioned.

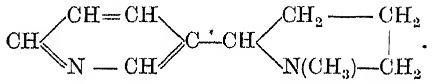
In order, however, that local anæsthesia may be efficacious and lasting, it is necessary to prevent the anæsthetic inoculated at a certain place from being carried away (*resorbed*) by the blood, and this was at first attained by causing the venous blood at that place to stagnate by preventing circulation. The same end was reached later by intense local cooling produced by the rapid evaporation of *ethyl* or *methyl chloride*.

For internal surgical operations (*e.g.*, in the thorax, etc.), *adrenaline*, $C_6H_3(OH)_2 \cdot CH(OH)$ $CH_2 \cdot NH \cdot CH_3$, is of the greatest use, as it produces considerable contraction of the blood-vessels without driving all the blood from them, although it prevents fresh blood from arriving; the anæsthetic can thus be kept as long as is desired in the inoculated region. The substitution of cocaine by *stovaine* (less poisonous) leads to partial *spinal anæsthesia* or medullary anæsthesia,

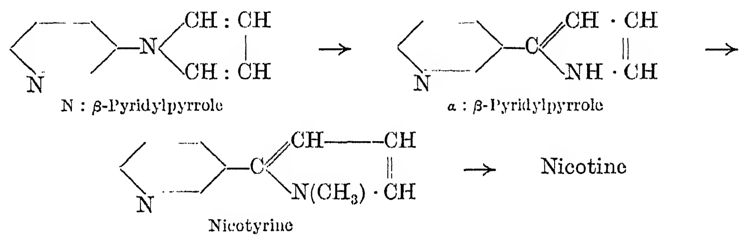
alkaloids in plants (*e.g.*, in Datura and tobacco) may be increased up to 30 per cent. by inoculating the plants with pyridine tartrate, which undergoes complete transformation into alkaloids. Salicylic alcohol injected into maize plants yields salicin and in general chemical compounds inoculated are found in the plants, not in the free state, but converted into glucosides. Thus, the plant protects itself against the poisonous action of these substances by converting them into innocuous compounds. These observations explain why the powerful alkaloids produced in certain plants as waste products of the decomposition of complex nitrogenous substances exert no harmful action on the plants, although in the free state they exercise serious effects on the animal organism, which is not able to immunise itself. Inoculation of plants with non-nitrogenous substances may also increase the formation of alkaloids, injection of glucose into tobacco increasing the amount of nicotine formed by 40 per cent.

CONIINE, $C_8H_{17}N$, is found in hemlock (*Conium maculatum*). For its constitution and syntheses, *see above*.

NICOTINE, $C_{10}H_{14}N_2$, is a strong diacid base which, in combination with malic and citric acids, forms the poisonous alkaloid of tobacco. It is an oil boiling at 247° and possessing a very strong odour; it is soluble in water, alcohol, or ether, and turns brown in the air. When oxidised by permanganate it forms nicotinic acid, and as further it contains also a pyrrolidine group, its constitution is represented as follows:



Synthetically it is obtained from β-aminopyridine which is converted into its mucic acid salt, and then passes through the following stages:



Practically it is prepared from ordinary tobacco extract, by diluting, rendering strongly alkaline with NaOH, and extracting with ether. From the ethereal solution, the alkaloid is extracted by shaking with dilute sulphuric acid and decanting off the acid solution. The latter is again made strongly alkaline and shaken with ether, and the ethereal solution dehydrated by means of solid NaOH. The ether is then distilled off and the remaining nicotine distilled in a stream of hydrogen.

It is a very powerful poison and is used medicinally to counteract nervous irregularity

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which now permits the most difficult surgical operations on the abdominal organs and even renders possible painless childbirth.

Adrenaline or *suprarenine*, $OH\langle C_6H_3 \rangle(OH)CH(OH) \cdot CH_2 \cdot NH \cdot CH_3$, was extracted from the suprarenal gland in 1901 by Takamine. Synthetically it may be prepared in various ways, *e.g.*, treatment of chloracetocatechol (from catechol and chloracetic acid) with excess of methylamine gives methylaminoacetocatechol (*adrenalone*), and reduction of the latter forms racemic adrenaline, which is less active than the natural lævo-rotatory compound; separation of the optical antipodes is effected by preparing the *d*-tartrate, the salt of the lævo-base being only slightly soluble in methyl alcohol. Nagai (1919) treats diacetylprotocatechualdehyde with nitromethane (1 mol.) in presence of a weak alkali; the diacetoxyphenylnitroethanol, $C_6H_3(O \cdot CH_3CO)_2 \cdot CH(OH) \cdot CH_2 \cdot NH_2$, formed being crystallised, washed with ether, and treated with zinc and acetic acid in presence of formaldehyde. Simultaneous reduction and methylation then occur, giving diacetyladrenaline. The zinc is removed as sulphide, and hydrolysis of the diacetyl compound effected by means of hydrochloric acid.

of the heart and is employed in agriculture, as tobacco extract, to kill insects.[1] Impure 75 per cent. nicotine cost before the war 148*s.* per kilo, and the pure product 184*s.* The French and Italian Governments place at the disposal of agriculturists *tobacco extract* (2 to 10 per cent. of nicotine) at about 2*s.* 6*d.* per kilo (pre-war).

[1] Tobacco is a herbaceous plant, originally an annual but now sometimes a biennial, of the order Solonaceæ (*Nicotiana tabacum*), which includes about fifty species and sub-species of American origin, *e.g.*, the Virginia tobacco plant (*Nicotiana tabacum*, *see* Fig. 466), the Maryland large-leaved tobacco (*N. latissima*, *N. rustica*, *N. suffruticosa*, etc.). These grow well in various countries, as is shown by the following Table, giving the mean production of raw tobacco a few years ago (the figures given are tons):

	Output	Imports less Exports	Exports less Imports
United States . .	250,000	—	115,000
British India . .	185,000	—	—
Austria-Hungary .	70,000	14,000	—
Russia . . .	58,000	—	5,000
Turkey . . .	40,000	—	14,000
Germany . .	37,000	45,000	—
(*a*) Belgium, (*b*) Algeria, (*c*) Australia, (*d*) Porto Rico, (*e*) Roumania, (*f*) San Domingo, (*g*) Ceylon, each about . . .	5,000	(*a*) 10,000 (*c*) 5,000 (*e*) 1,300	(*d*) 4,500 (*f*) 3,000 (*g*) 3,000
(*a*) Italy, (*b*) Switzerland, (*c*) Servia, (*d*) Sweden, each from 1,500 to . .	2,300	(*b*) 5,000 (*c*) 1,000 (*d*) 4,300	

	Output	Imports	Exports
Dutch Indies . .	34,000		18,000
Japan . . .	26,000		
France . . .	25,000	23,000	. .
Cuba . . .	21,000		13,500
Philippines . .	22,000		12,000
Brazil . . .	17,000		11,000
Greece . . .	9,000		5,000
(*a*) Bosnia, (*b*) Netherlands, (*c*) Argentine, (*d*) Cochin China, (*e*) Mexico, each about . .	3,300	(*c*) 5,200	
(*a*) China, (*b*) Paraguay and other countries, together	120,000		(*a*) 5,500 (*b*) 5,000
Great Britain . .	--	50,000	

Italy imported before the war about 2000 tons of tobacco leaf (about £1,080,000) and exported manufactured tobacco to the value of about £200,000.

The world's pre-war production of raw tobacco varied from 900,000 to 1,000,000 tons, of the value of £48,000,000 to £56,000,000. The price was about £32 to £40 per ton for the ordinary quality and £120 to £160 for the finer qualities (Manila, Havana, Sumatra).

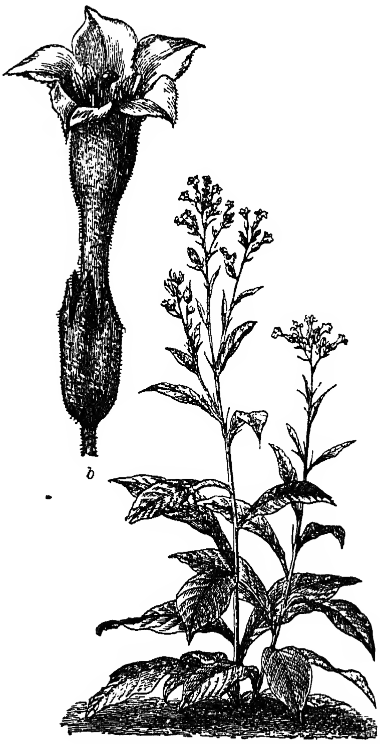


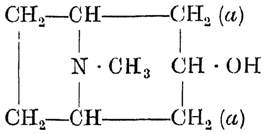
FIG. 466.

Ordinary tobacco plants are only slightly branched and have a height of about 1 metre, although some exceed 1½ metre. They are studded with sticky hairs, and the leaves are wide and oval or, sometimes, long and narrow, as with Chinese tobacco (*N. chinensis*). The flowers are in clusters and resemble those of potatoes, but are usually flesh-red. The cultivation of tobacco requires a good soil rich in humus, and the climate, soil, and mode of growing exert a considerable influence on the quality of the tobacco. The readiness with which a tobacco burns in the form of cigars depends on the potash-content of the plant, while chlorides hinder the combustion. On this account fertilisation with stable manure, sewage, or potassium chloride is avoided, preference being given to potassium or ammonium sulphate mixed with a little Thomas slag and stable manure. The young plants from the forcing house are planted out in about March, and at the beginning of July the dry and dirty leaves near the soil are detached, together with the useless branches and the flowers. The other, useful leaves are then removed as they begin to yellow and are dried on strings or in steam drying-ovens, and are then sorted and tied in bundles.

In January the leaves are placed in heaps so as to induce fermentation, which renders them brown and gives them flavour.

The leaves arrive at the factory in cloth bales. They are first sorted into kinds suitable for different types of tobacco and are then beaten to remove sand and dust. They are then arranged in layers, each of which is sprinkled with 5 to 10 per cent. salt solution (it is this which renders cigars hygroscopic) to soften it, to facilitate the subsequent operations and to prevent putrid fermentation. In this state it is sometimes placed in tepid apartments to initiate a second

ATROPINE, $C_{17}H_{23}O_3N$, is the alkaloid of the berries of *Atropa belladonna* (deadly nightshade) and of the fruit of *Datura stramonium* (thorn-apple). In dilute solution it is used as a mydriatic (enlarging the pupil of the eye) and as an analgesic (relieving pain). It is somewhat poisonous and melts at 115·5°. As the products of the decomposition of atropine in various ways comprise heptamethylene derivatives, substituted pyrrolidines and piperidines, **tropine**, $NC_8H_{15}O$, and **tropic acid** [$C_9H_{10}O_3$, or α-phenyl-β-hydroxypropionic acid, $OH \cdot CH_2 \cdot CH(C_6H_5) \cdot CO_2H$], atropine is regarded as an ester, a tropate of *tropine*, the structure of the latter (which has also been prepared synthetically) being,



(m.-pt. 62° ; b.-pt. 220°).

Hyoscyamine, stereoisomeric with atropine, melts at 109°.

Tropine, formed by the splitting of atropine with barium hydroxide, is a tertiary base containing a secondary alcoholic group and is therefore known also as *tropanol*. When oxidised with chromic acid, it forms first a ketone, **tropinone**, $C_8H_{13}ON$, and then **tropinic acid**, $CH_3N : C_4H_6(CO_2H)(CH_2 \cdot CO_2H)$, owing to the rupture of the piperidine ring. With

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fermentation, which refines the milder qualities ; in some cases this end is attained by washing with dilute solutions of salts, alkali, or acid, or, more rarely, by torrefying at 60° to 70°.

The best flavour and aroma are obtained, however, by *curing*, *i.e.*, by immersing the leaf in an aqueous solution of saccharine substances, various drugs, nitre, colouring-matters, aromatic substances, alcohol, etc. (each manufacturer has his particular method of curing) ; the drained or pressed leaves are then left in heaps for a longer or shorter time until they are uniformly soaked.

By suitable machines the ribs of the leaves are either cut or beaten off and the cut leaves then dried by heating in revolving metal drums ; the dried leaves are rapidly cooled in a current of air, etc. The subsequent operations for the preparation of cigars, cigarettes, cut tobacco for pipes, or snuff are merely mechanical and need not be described here.

Mention may, however, be made of recent attempts to diminish the harmful effects of tobacco, which is now smoked in every country in the world. It seems that when the Spaniards invaded America, the use of tobacco was already known in that country, and they not only extended its use there but introduced it into Europe (by the Thévet brothers in 1517), arousing grave apprehension owing to a statement by the medical men that it was highly injurious to health. In 1613 Tsar Michael Federowitz prohibited its use in his territory under penalty of death or of the cutting off of the nose. James I. of England published in 1619 a decree forbidding the use of tobacco and describing smoking as a " habit disgusting to the sight, nauseating to the smell, dangerous to the brain, harmful to the heart, and spreading around the smoker repugnant exhalations." In 1660 the Senate of Berne punished the use of tobacco like robbery or homicide, and in 1623 Amurat IV. prohibited its use by the Turks in order that they might not become intoxicated or infertile. To human nature, however, the forbidden fruit is the most desired, and, being useless, is none the less necessary. The employment of tobacco spread rapidly everywhere, and many States, to limit its consumption, imposed enormous taxes on tobacco, and ended by making it a Government monopoly and thus deriving a vast income to the Treasury.

Since then no Government has occupied itself with the health of its subjects, the only care being the enlargement of the Exchequer. In Italy, after the partnership between the Government and a private company from 1868 to 1883, the trade in tobacco became a monopoly of the State, which derived from it a net annual income of about £7,000,000 (pre-war ; in 1920 far more).

The mean yearly pre-war consumption of tobacco per head was as follows: North America, 3·1 kilos ; Netherlands, 2·5 ; Belgium, 2·8 ; Switzerland, 2·3 ; Germany, 1·5 ; Austria-Hungary, 1·5 ; Sweden, 1·2 ; Russia, 0·9 ; Servia, 0·8 ; France, 0·8 ; England, 0·7 ; Italy, 0·6 ; Roumania, 0·2 ; Denmark, 0·1 ; Finland, 0·1.

The harm caused by tobacco is due especially to the nicotine, to which man becomes accustomed without serious inconvenience, in the same way as to change of climate, food, drink, or other conditions. Attempts have been made in recent years to render tobacco less injurious by extraction of the nicotine with one of a number of solvents, but such treatment results in the removal of the aromatic substances of the tobacco (*see also* Ger. Pats. 178,962, 197,159, and 212,410 of 1908).

Better results are obtained by filtering the smoke through fibres or textile materials before it reaches the mouth. Thus the Thoms process (Ger. Pat. 145,727), which has proved very satisfactory, consists in arranging in the mouthpiece of the pipe a small plug of cotton-wool impregnated with ammoniacal ferric chloride or ferrous sulphate, this retaining all the burning ethereal oils, the hydrogen sulphide, a considerable proportion of the hydrocyanic acid, and almost all the nicotine and its basic derivatives in the smoke. Treating the raw tobacco with ozone has also been employed with the view of facilitating the elimination of the nicotine, increasing the combustibility, and improving the quality. The aroma of tobacco is also intensified by the addition of small quantities of methyleugenol and methylisoeugenol.

concentrated HCl, tropine forms tropidine (or *tropene*), $C_8H_{13}N$, which is obtained also by elimination of CO_2 from anhydroecgonine and forms an oily base, b.-pt. 162°.

OTHER ALKALOIDS are: Veratrine (*cevadine*), $C_{32}H_{29}O_9N$, found in *Veratrum album*; Sparteine, $C_{15}H_{26}N_2$, found in *Sparticum scoparium*; Sinapine, $C_{16}H_{25}O_6N$, found in the seeds of white mustard and derived from choline and from sinapic acid (*dimethyltri-hydroxycinnamic acid*), $C_{11}H_{12}O_5$; Hydrastine, $C_{21}H_{21}O_6N$, obtained from the roots of *Hydrastis canadensis*, has similar properties to the alkaloid from *Secale cornutum* and gives hydrastinine, $C_{11}H_{11}O_2N,H_2O$, on oxidation.

MORPHINE, $C_{17}H_{19}O_3N$. The latex of the capsule of *Papaver somniferum* when condensed forms opium, which, along with various other compounds (*see below*), contains considerable quantities of *morphine* (about 10 per cent.). Morphine, melting and decomposing at 230°, is slightly soluble in water and odourless, and possesses narcotic and analgesic properties, being used in medicine as hydrochloride, $C_{17}H_{19}O_3N,HCl,3H_2O$. It is a tertiary base with phenolic characters and, when distilled in presence of zinc dust, gives pyridine, pyrrole, quinoline, and phenanthrene.

Morphine is extracted from opium by means of water, the evaporated aqueous extract being treated with sodium carbonate to precipitate all the alkaloids (about twenty) of the opium; after 24 hours the precipitate is washed with water and then with alcohol, which removes the resins and all the alkaloids excepting nearly the whole of the morphine. The crude morphine remaining is dissolved in acetic acid (which leaves behind the narcotine impurities), the solution filtered through animal charcoal, and the morphine liberated by means of ammonia, washed with cold water and dried. It is obtained in a purer form by repeatedly boiling its alcoholic solution with animal charcoal and recrystallising.

The action of opium on the human organism is analogous to that of other stupefying agents, being intermediate to that of alcohol, ether, etc., and that of cocaine. The smoking of opium, either alone or together with tobacco, is a habit which has been long rooted in certain countries, especially China.

The action of opium is due to the presence of a number of alkaloids, which are divided by A. Pictet into:

(1) The **Morphine Group**, including:

Morphine, $C_{17}H_{17}ON(OH)_2$	*Codeine*, $C_{17}H_{17}ON(OH)(OCH_3)$
Pseudomorphine, $[C_{17}H_{16}ON(OH)_2]_2$	*Thebaine*, $C_{17}H_{15}ON(OCH_3)_2$

(2) The **Papaverine Group**, comprising mainly isoquinoline derivatives, which have a mild physiological action:

Papaverine, $C_{16}H_9N(OCH_3)_4$	*Laudamine*, $C_{17}H_{15}N(OH)(OCH_3)_3$
Laudanidine, $C_{17}H_{15}N(OH)(OCH_3)_3$	*Laudanosine*, $C_{17}H_{15}N(OCH_3)_4$
Codamine, $C_{18}H_{18}ON(OH)(OCH_3)_2$	*Cryptopine*, $C_{19}H_{17}O_3N(OCH_3)_2$
Narcotine, $C_{19}H_{14}O_4N(OCH_3)_3$	*Oxynarcotine*, $C_{19}H_{14}O_5N(OCH_3)_3$
Protopine, $C_{20}H_{19}O_5N$	*Narceine*, $C_{20}H_{18}O_5N(OCH_3)_3$
Tritopine, $(C_{21}H_{27}O_3N)_2O$	*Meconidine*, $C_{21}H_{23}O_4N$
Papaveramine, $C_{21}H_{21}O_5N$	*Gnoscopine*, $C_{22}H_{33}O_7N$
Santaline, $C_{37}H_{36}O_9$	*Hydrocotarnine*, $C_{11}H_{12}O_2N(OCH_3)$
Lautopine, $C_{23}H_{25}O_4N$	*Berberine*, $C_{20}H_{17}O_4N$

Opium contains also **Meconic Acid**, $C_7H_4O_7$, in combination with various alkaloids, and further: wax, proteins, caoutchouc, pectic and gummy matters, lactic and sulphuric acids, ammonium salts, etc.

Good opium contains 8 to 24 per cent. of water, 3·5 to 5 per cent. of ash, 45 per cent. of aqueous extract, 9 to 15 per cent. of morphine, about 5 per cent. of narcotine, 0·8 per cent. of papaverine, 0·4 per cent. of thebaine, 0·3 per cent. of codeine, and 0·2 per cent. of narceine.

The pre-war price of good opium was 28*s*. to 32*s*. per kilo, pure crystalline morphine costing £24 and its hydrochloride £18 per kilo. In 1905 Germany imported 68 tons of opium of the value of £80,000. China imported 2600 tons in 1908, about 2500 in 1909, and nearly 2000 in 1910. In 1910 Great Britain imported about 220 tons of opium and in 1911 exported 22 tons. The United States imported 300 tons in 1911.

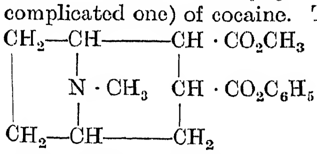
COCAINE, $C_{17}H_{21}O_4N$, is obtained, together with other alkaloids (**Cinnamylcocaine, Cinnamylecgonine, α-Truxilline, Hygrine**, etc.), from the leaves of a small shrub (*Erythroxylon coca*) which grows abundantly in Peru, Bolivia, Colombia, Brazil, and Argentine and is now cultivated also in Ceylon and Java. Peru and Bolivia alone produce annually

about 15,000 tons of dry *coca leaves* containing 0·5 to 2·6 per cent. of various alkaloids, including 0·2 to 0·8 per cent. of cocaine. The leaves are mostly used by the natives, who chew them, and are partly treated on the spot for preparing crude cocaine containing 80 to 90 per cent. of cocaine and 10 to 12 per cent. of other alkaloids, this being marketed at Hamburg and London. Before the war the dry leaves were sold in London at about £4 per cwt.

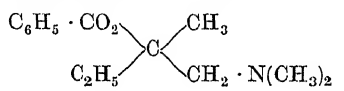
Not only cocaine, but also the other alkaloids accompanying it in coca leaves, are derived from a single base *ecgonine*.

Pure cocaine, m.-pt. 98°, is lævo-rotatory and has an analgesic action; it is used in opthalmology and surgery to effect local anæsthesia, and is employed by drug-takers owing to its stupefying action.

Strong acids in the hot decompose it into methyl alcohol, benzoic acid and *ecgonine*, $C_9H_{15}O_3N$ (Lossen, 1865), which is the α-carboxyl derivative of tropine (*see above*), and, as with methyl alcohol and benzoic acid it gives cocaine again, the latter must contain the groups $C_9H_{13}O_2N\begin{cases}OCH_3\\COC_6H_5\end{cases}$; confirmation of this is given by the synthesis (rather a complicated one) of cocaine. The constitution of cocaine is as follows (Willstätter, 1898):

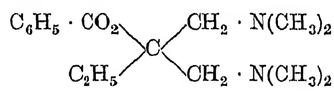


; the characteristic group (*anæsthesiophore*) is the benzoyl residue, while elimination of the methyl group united to the nitrogen atom or of the CO_2CH_3 group scarcely affects the anæsthetic properties. On the other hand, almost all the amino-hydroxybenzoic esters are *mild local anæsthetics* (Einhorn and Heinz, 1897), *e.g.*, *anæsthesin* or ethyl p-aminobenzoate, $NH_2 \cdot C_6H_4 \cdot CO_2C_2H_5$. The anæsthetic characters of these substances are intensified if, in place of NH_2, $N(CH_3)_2$ groups are present, preferably joined to other methyl groups. This is the case, for instance, in:



Stovaine

and

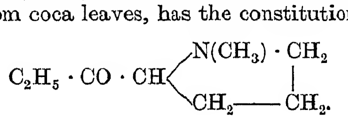


Alypine

prepared by Messrs. Bayer in 1905. Both of these are less poisonous than cocaine, but have not its property of contracting the blood-vessels. They are therefore mixed with *adrenaline*, which shows this property in a marked degree and also diminishes the toxicity of certain alkaloids, especially of cocaine.

The price of cocaine was about £800 per kilo prior to 1885, £140 in 1887, £22 in 1906, and £12 in 1913. During and after the war the price rose enormously. Owing to the high price of cocaine, many substitutes have been prepared; of these a few have been successfully used, such as *β-eucaine* (trimethyl-γ-oxypiperidine *o*-benzoate); *holocaine*, obtained by condensing phenacetin with p-phenetidine (in spite of its lack of the benzoyl anæsthesiophore group); *acoine* (di-p-anisyl-p-phenetylguanidine), etc.

HYGRINE, obtained from coca leaves, has the constitution—



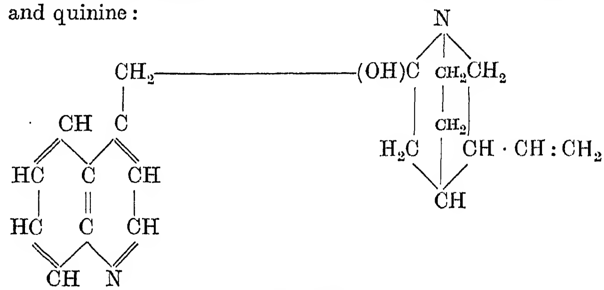
NARCOTINE, $C_{22}H_{23}O_7N$, exists to the extent of 6 per cent. in opium, melts at 126°, and is a slightly poisonous, weak, tertiary base containing three methoxyl groups. When hydrolysed, narcotine gives **meconic anhydride**, $C_{10}H_{10}O_4$, and **cotarnine**, $C_{12}H_{13}O_3N$, which is a derivative of isoquinoline (*see later*), and with bromine gives dibromopyridine.

STRYCHNINE, $C_{21}H_{22}O_2N_2$, is present, with **brucine**, $C_{23}H_{26}O_4N_2$, and **curarine**, in the seeds of *Strychnos nux vomica*. They are very powerful poisons, which, even in small doses, cause death, accompanied by tetanic muscular contorsions; curarine is used as an antidote to the other two alkaloids. Strychnine melts at 265°, and is a mono-acid tertiary base slightly soluble in water; it gives indole and quinoline when fused with potash and β-picoline on distillation with lime.

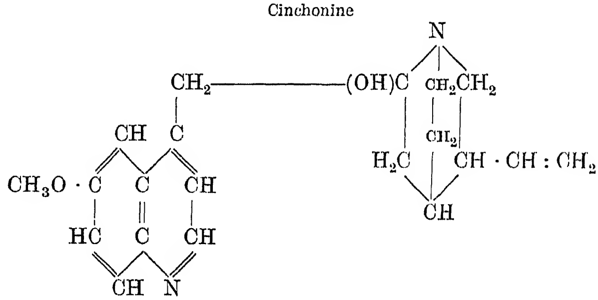
QUININE, $C_{20}H_{24}O_2N_2$. The bark of various species of cinchona has yielded, up to the present, twenty-four alkaloids, the most important being quinine and cinchonine,

$C_{19}H_{22}O_2N_2$, both of these possessing in different degrees febrifugic properties. The other alkaloids include **Hydroquinine**, $C_{20}H_{26}O_2N_2$; **Cinchonidine**, $C_{19}H_{22}ON_2$; **Hydrocinchonidine**, $C_{19}H_{24}ON_2$; **Quinidine**, $C_{20}H_{24}O_2N_2$, etc.

Quinine is lævo-rotatory, slightly soluble in water and odourless and has an intensely bitter taste; it melts at 177°, or, when crystallised with $3H_2O$, at 57°. It is a di-acid base, containing two tertiary nitrogen atoms capable of salt-formation with two equivalents of acid, then often giving aqueous solutions showing blue fluorescence characteristic of quinine. It contains a hydroxyl and a methoxyl group, and its constitutional formula, although not completely established, must consist of two cyclic systems, $NC_{10}H_{15}(OH) - NC_9H_5 \cdot OCH_3$, the first being somewhat analogous to tropine (*see above*) and the second representing 5-methoxyquinoline, which can be obtained by fusing quinine with potash. After protracted investigation, W. Königs (1906–1907) arrived at the following probable structures for cinchonine and quinine:

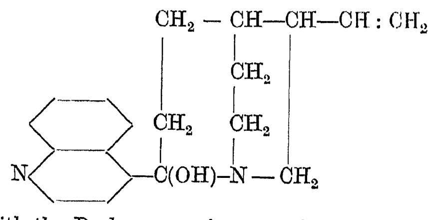


Cinchonine



Quinine

Rabe (1906–1907), however, proposed for cinchonine the formula:



which is in harmony with the Beckmann oxime reaction.

Oxidation of quinine gives, among other products, Quinic acid, $C_9H_5N(OCH_3) \cdot CO_2H$.

To combat fever, especially malarial fever, use is made of the *normal sulphate of quinine*, $(C_{20}H_{24}O_2N_2)_2,H_2SO_4,8H_2O$ (from alcohol it crystallises with $2H_2O$), or of *quinine hydrochloride*, $C_{20}H_{24}O_2N_2,HCl,2H_2O$, which is far more readily soluble in water.

Quinine bisulphate or acid sulphate contains 1 mol. of quinine per 1 mol. of sulphuric acid.

Quinine is extracted from the finely ground bark by mixing it with lime and extracting with hot mineral oils (paraffin oil, etc.) of high boiling-point. From this solution the alkaloid is obtained by shaking with dilute sulphuric acid, neutralisation of the acid solution with sodium carbonate in the hot resulting in the crystallisation of most of the quinine as sulphate from the cold solution, the other alkaloids remaining dissolved. From the sulphate the quinine is liberated by means of ammonia.[1]

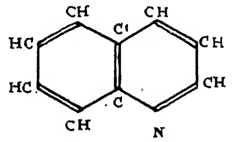
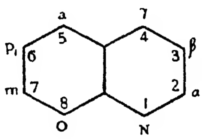
[1] Since quinine and its true salts are very bitter, attempts have been made to prepare less bitter compounds. In 1896 tasteless *euquinine*, or quinine ethyl carbonate, $(C_{20}H_{23}ON_2)$

The purification of quinine is not easy and is sometimes effected by precipitating it from solution as tartrate by addition of Rochelle salt.

STATISTICS. Before the war quinine bisulphate cost about 28*s.* per kilo, the sulphate 32*s.*, and the hydrochloride 40*s.* The world's output of cinchona bark was 12,000 tons in 1916.[1]

5. QUINOLINE AND ITS DERIVATIVES

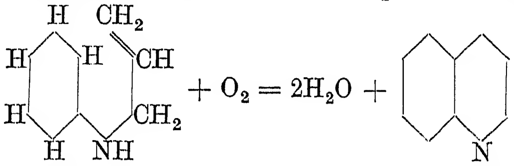
Quinoline and pyridine are related in the same way as naphthalene and benzene.

QUINOLINE, C_9H_7N, *i.e.*,  or , is a highly refractive, colourless liquid of peculiar odour and is found in bone tar and also in coal-tar, but is now prepared in the pure state by Skraup's synthesis.

It is slightly soluble in water, has the sp. gr. 1·1081 at 0°, boils at 236° and functions as a tertiary base (the nitrogen not being combined with nitrogen). With acids it forms salts, *e.g.*, the bichromate $(C_9H_7N)_2H_2Cr_2O_7$.

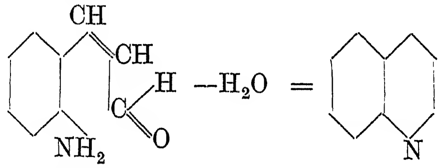
Its constitution is deduced from the following syntheses:

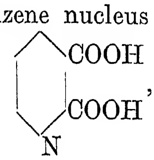
(1) By the interaction of **allylaniline** and PbO_2 at a red heat:



(2) Skraup obtained it by heating aniline with glycerol, sulphuric acid, and nitrobenzene; in this way acroleïn is formed, which then gives **acroleïn-aniline**, $C_6H_5 \cdot N : CH \cdot CH : CH_2$. The nitrobenzene acts purely as an oxidising agent and may be replaced by As_2O_3. Margosches (1904) suggested the replacement of the nitrobenzene by rare oxides of the cerium group.

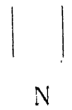
(3) *o*-Nitrocinnamaldehyde on reduction gives *o*-aminocinnamaldehyde, which loses 1 mol. H_2O and yields quinoline, the fact that the latter is an ortho-derivative of benzene being thus proved:



When quinoline is oxidised, the benzene nucleus is attacked first, with formation of a dibasic **quinolinic acid**, , which gives pyridine,

$(C_2H_5)CO_3$, was placed on the market (Zimmer, Ger. Pats. 91,370 and 118,352), and in 1902, *aristoquinine* (*aristochin*), or quinine carbonate, $(C_{20}H_{23}ON_2)_2CO_3$ (Bayer and Zimmer, Ger. Pat. 105,666, 1898). It was claimed that 2 grms. of either of these products has the effect of 1 grm. of quinine. Biginelli (1914) showed, however, that they are not salts of carbonic acid, that true quinine carbonate is very bitter, that their action on the organism is slight and slow compared with that of quinine, and that euquinine is ethyl quininecarboxylate, $C_{20}H_{23}O_2N_2 \cdot COOC_2H_5$, and aristochin, carbonylquinine, $(C_{20}H_{23}O_2N_2)_2CO$.

[1] At one time cinchona was cultivated extensively in Ceylon, but, owing to over-production in 1885 and consequent lowering of prices, it was abandoned and replaced by rubber. In Southern India, however, the industry increased, 1050 tons of the bark being exported in 1914, and nearly 900 tons in 1916. In Java the production commenced in 1879, 3000 tons of bark being exported in 1889, 9500 tons in 1910, and about 10,500 tons in 1915.

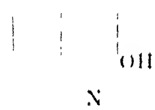
, when distilled with lime. Hence, as was suggested long ago by Korner, quinoline contains a benzene and also a pyridine nucleus. It is analogous to naphthalene, one α CH group being replaced by a nitrogen atom. That the linkings in quinoline are, at least in part, olefinic double bonds is shown by the behaviour of this compound to ozone.

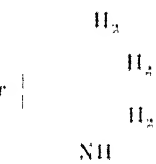
Quinoline forms many isomeric derivatives, seven monosubstituted, twenty one disubstituted, and still more trisubstituted compounds being possible.

The positions of the replaceable hydrogen atoms are indicated by numbers or by the letters α, β, and γ for the pyridine nucleus and *o*, *m*, *p*, *a* (ortho-, meta-, para-, ara-) for the benzene nucleus.

The constitution of quinoline derivatives can be determined by means of the general synthesis of Skraup, variously substituted anilines with the substituents in the benzene nucleus being used; or often by oxidation, which usually attacks the benzene nucleus and not the pyridine nucleus, so that it is easily ascertained whether the substituent is in the one or the other nucleus.

The *sulpho-acids* (or sulphonic acids) of quinoline, when fused with KOH, give *hydroxyquinolines*, and these, on being heated with KCN, form *cyanoquinolines*, which are converted by hydrolysis into the corresponding *quinolinecarboxylic acids*, those containing the carboxyl in the benzene nucleus are called *quinolinbenzocarboxylic acids*. Oxidation of cinchonine gives *cinchonic acid*, $C_9H_6N \cdot CO_2H$ (m. pt. 254°), which is *quinoline-γ-carboxylic acid*, and from this is derived *quinic acid (see above)*, $C_9H_5N(OCH_3) \cdot CO_2H$ (*p* : γ), consisting of yellow prisms melting at 280°. When acridine is oxidised it yields *quinoline α : β dicarboxylic acid* or *acridic acid*.

Carbostyril is 2-hydroxyquinoline, , and has the character of the phenols, dissolving in alkali and being reprecipitated by CO_2, etc.

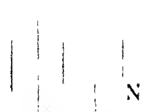
When quinoline is reduced with nascent hydrogen, this unites with the nitrogenated nucleus, forming **tetrahydroquinoline**, $C_9H_{11}N$, or , which behaves as a secondary aromatic amine ($>$NH).

If the reduction is pushed further, the hydrogen is added also to the benzene nucleus, forming *decahydroquinoline*, $C_9H_{17}N$, which behaves like an aromatic amine.

Quinaldine or α-**methylquinoline**, $C_{10}H_9N$, is found in coal tar and boils at 246°; with phthalic anhydride it gives a fine colouring matter, **quinoline yellow**, $C_{10}H_7N(CO)_2C_6H_4$.

When quinoline is heated with metallic sodium it gives *diquinolyl*, $C_9H_6N \cdot C_9H_6N$, analogous to dipyridyl and diphenyl. Polymerisation of quinoline yields *diquinoline*, $(C_9H_7N)_2$, crystallising in yellow needles.

METHOXYQUINOLINE, $C_9H_6N \cdot OCH_3$, corresponding with anisole, resembles quinoline; among its derivatives are the antipyretic, **thalline**, $C_9H_{10}N \cdot OCH_3$, and **analgen** (*o*-ethoxy-α-benzoylaminoquinoline).

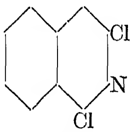
ISOQUINOLINE, C_9H_7N or , is a colourless liquid boiling at 237°, melting at 21° and forming a slightly soluble sulphate.

It is obtained from tar and also synthetically by heating the ammonium salt of homophthalic acid:

$$C_6H_4\left\langle\begin{array}{l}CH_2\cdot COONH_4\\ \\ COONH_4\end{array}\right. = 2H_2O + NH_3 + C_6H_4\left\langle\begin{array}{l}CH_2\cdot CO\\ \qquad |\\ CO\cdot NH\end{array}\right.,$$

Homophthalimide

which with $POCl_3$ gives $C_6H_4\left\langle\begin{array}{l}CH_2\cdot CCl_2\\ \qquad |\\ CCl_2\cdot NH\end{array}\right.$, and elimination of 2HCl from this yields



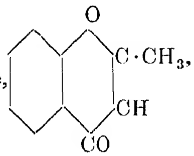
, *i.e.*, dichloroisoquinoline.

When oxidised it gives phthalic acid and **cinchomeronic acid**, $C_5H_3N(CO_2H)_2$ (a pyridine derivative).

Since it does not fix ozone, it must be assumed, contrary to the former view, that it does not contain olefinic double linkings, but that centric bonds are probably present in both nuclei (Molinari, 1907).

Other condensed nuclei, similar to quinoline, are as follow:

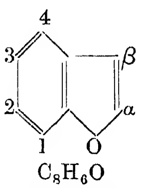
CHROMONE, $C_6H_4\left\langle\begin{array}{l}O\cdot CH\\ \qquad \|\\ CO\cdot CH\end{array}\right.$, of which the β-methyl-derivative,



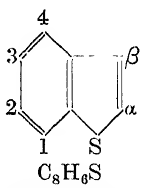
m.-pt. 71°, is well known.

FLAVONE, the phenyl-derivative of *chromone*, $C_6H_4\left\langle\begin{array}{l}O\cdot C\cdot C_6H_5\\ \qquad \|\\ CO\cdot CH\end{array}\right.$, melts at 97°, and occurs as hydroxy-derivatives in many glucosides, to which it imparts the yellow coloration. Thus it occurs in *quercetin* (or *flavin*), which is a pentahydroxyflavene, while with isodulcitol it forms the glucoside **quercitrin**, $C_{21}H_{23}O_{12}$, obtained from tea, hops, and the bark of *Quercus tinctoria* (*morin* is an isomeride of quercetin, and is found in *Maclura tinctoria*). **Chrysin**, $C_{15}H_{10}O_4$, is a dihydroxyflavone found in poplar buds; **Luteolin**, $C_{15}H_{10}O_6,2H_2O$, is a tetrahydroxyflavone, and forms the colouring-matter of *Reseda luteola*, while *apigenin* is a glucoside of trihydroxyflavone, and is found in parsley and celery.

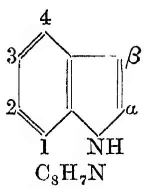
Of the many condensed cyclic groups, the following, which contain a benzene nucleus and also a furfuran, thiophen or pyrrole nucleus, and are obtained by various syntheses, may be mentioned:



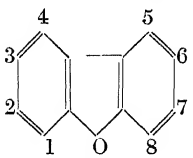
C_8H_6O
Coumarone or Benzofurfuran



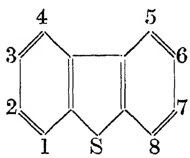
C_8H_6S
Benzothiophen or Thionaphthene



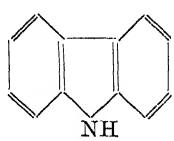
C_8H_7N
Indole or Benzopyrrole



$C_{12}H_8O$
Diphenylene oxide or Dibenzofurfuran



$C_{12}H_8S$
Diphenylene sulphide or Dibenzothiophen



$C_{12}H_9N$
Diphenyleneimine, Dibenzopyrrole, or Carbazole

Of all these groups numerous halogenated, acid, alcoholic, ethereal derivatives, etc. are known.

COUMARONE is a liquid, b.-pt. 177°, is obtained synthetically, and also, together with

various methylcoumarones, from coal-tar. Concentrated sulphuric acid polymerises it to coumarone resin, which, on dry distillation, yields coumarone and phenol with partial charring. At 200°, alcoholic potash opens the smaller nucleus, various products being formed. It readily unites with two halogen atoms. *a*-Bromocoumarone loses bromine and yields *a*-nitrocoumarone, m.-pt. 134°, when treated with N_2O_3.

BENZOTHIOPHEN, m.-pt. 32°, b.-pt. 221°, occurs in lignite tar.

Of numerous dyestuffs formed by the condensation of heterocyclic groups, mention will be made later in the chapter on *colouring-matters*, but a group of substances with heterocyclic nuclei and intimately connected with indigo will be considered here.

ISATIN, $C_6H_4{<}{}^{NH}_{CO}{>}CO$, forms reddish yellow prisms soluble in alcohol and in hot water, and may be regarded as the *lactam* (*see* p. 423) of Isatinic acid, $NH_2 \cdot C_6H_4 \cdot CO \cdot COOH$. It is obtained from *o*-nitrobenzoylformic acid (*see later*, Indole), by oxidising indigo with nitric acid, etc. It dissolves in KOH, giving first a violet colour ($C_6H_4{<}{}^{NK}_{CO}{>}CO$), while in the hot it yields potassium isatinate, $C_6H_4{<}{}^{NH_2}_{CO \cdot CO_2K}$. Oxidation of isatin with chromic acid gives rise to **Isatic acid** (anhydride of anthranilcarboxylic acid), $C_6H_4{<}{}^{NH \cdot CO}_{CO \cdot O}$ (NH · CO | CO · O).

From **Pseudoisatin**, $C_6H_4{<}{}^{CO}_{N}{>}C \cdot OH$ (which would be a *lactim*) is derived the methyl ether or **Methylpseudoisatin**, $C_6H_4{<}{}^{CO}_{N}{>}C \cdot OCH_3$ (red powder). **Methylisatin**, $C_6H_4{<}{}^{N(CH_3)}_{CO}{>}CO$, is also known.

DIOXYINDOLE, $C_6H_4{<}{}^{CH(OH)}_{NH}{>}CO$, is formed by reducing isatin with zinc and HCl and readily gives isatin again on oxidation. It is the internal anhydride of *o*-aminomandelic acid, and exhibits both basic and acid properties. It crystallises in colourless prisms, melting at 180°.

OXINDOLE, $C_6H_4{<}{}^{NH}_{CH_2}{>}CO$, acts both as an acid and as a base, and hence dissolves in alkali and in HCl. It is the lactam of *o*-aminophenylacetic acid, and can, indeed, be obtained by reducing *o*-nitrophenylacetic acid. It forms colourless needles, m.-pt. 120°, and forms dioxyindole on oxidation.

INDOXYL, $C_6H_4{<}{}^{NH}_{C(OH)}{>}CH$, is isomeric with the preceding compound, and is formed by fusing indigo with KOH or by the elimination of CO_2 from *indoxylic acid* or *indophore*.

It occurs in the urine of herbivorous animals in the form of **Potassium indoxylsulphate**, $C_8H_6N \cdot O \cdot SO_3K$ (*indican of the urine*). Derivatives of **Pseudoindoxyl**, $C_6H_4{<}{}^{NH}_{CO}{>}CH_2$, are also known.

SKATOLE, $C_6H_4{<}{}^{NH}_{C(CH_3)}{>}CH$, is formed during the putrefaction of protein or by fusing the latter with KOH, and is hence found in the fæces. It forms white scales, m.-pt. 95°, with an intense fæcal odour.

INDOLE, $C_6H_4{<}{}^{NH}_{CH}{>}CH$, is of importance owing to its intimate connection with indigo. By treating *o*-nitrobenzoyl chloride with AgCN, the nitrile is obtained and this, on hydrolysis, gives *o*-nitrobenzoylformic acid :

$$C_6H_4{<}{}^{COCl\ (1)}_{NO_2\ (2)} \rightarrow C_6H_4{<}{}^{CO \cdot CN}_{NO_2} \rightarrow C_6H_4{<}{}^{CO \cdot COOH}_{NO_2} ;$$

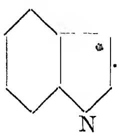
this acid, on reduction, gives the amine, which loses 1 mol. H_2O, forming Isatin :

$$C_6H_4\left\langle\begin{matrix}CO\cdot COOH\\ NH_2\end{matrix}\right. = H_2O + C_6H_4\left\langle\begin{matrix}CO\\ N\end{matrix}\right\rangle C\cdot OH.$$

Isatin

Indole is obtained by distilling oxindole with zinc dust and by various synthetical processes (*see later*, Indigo) ; it is formed in the pancreatic putrefaction of protein or on fusion of this with KOH. In the impure state it has a fæcal odour, but when pure and highly diluted it smells like flowers, and is hence used in perfumery. It forms shining scales which melt at 52°, are volatile in steam, and with ozone give indigo.

With sodium bisulphite it forms a crystalline compound, and with nitrous acid a red precipitate ; it imparts a red colour to a pine shaving moistened with HCl. It may be regarded as formed by the condensation of 1 mol. of benzene and 1 mol. of pyrrole :



. It forms numerous derivatives with substituents in the benzene or pyrrole nucleus, the two CH groups near the NH being termed α and β.

INDAZOLE, $C_6H_4\left\langle\begin{matrix}NH\\ CH\end{matrix}\right\rangle N$, is a weak base prepared by decomposing the diazo-compound of *p*-nitro-*o*-toluidine with acetic acid in the hot and then eliminating the NO_2 group.

INDIGO, $C_{16}H_{10}O_2N$, is a very stable, natural, blue colouring-matter, which was in use in the Far East in the most remote times, and was bartered to the Egyptians—mummies of the Eighteenth Dynasty (1580 years B.C.) are found with wrappings coloured with indigo—then to Greece, and later to Italy. Until the middle of the nineteenth century the trade in indigo remained a monopoly of the Dutch.

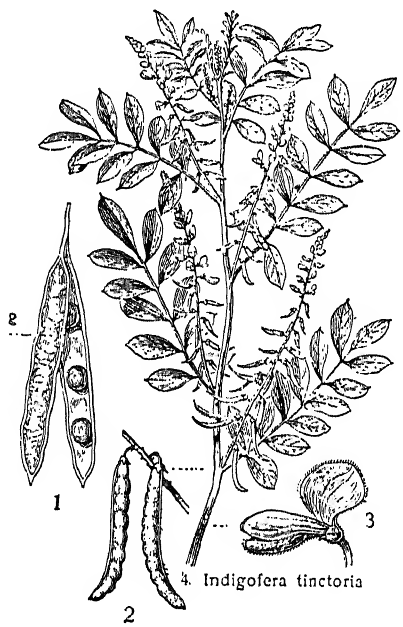


FIG. 467.

It is extracted from the branches and leaves (of a yellowish green colour) of *Indigofera tinctoria* (Fig. 467), which grows very readily in tropical countries and is extensively cultivated in India, Java, China, etc., being sown in the spring and cut two or three times a year before flowering.[1] At one time it

[1] Indigo belongs to the leguminous plants, and is hence capable of enriching the soil with nitrogenous products owing to the action of bacteria which fix atmospheric nitrogen (*see* Vol. I., p. 348). It has therefore been proposed to plant indigo in rotation with sugar-cane, especially in soils which have been exhausted by the latter. At every cutting 25 to 30 quintals of indigo plants are obtainable per hectare and 5 to 6 kilos of 60 per cent. indigo for every ton of plants.

In India indigo is sown in February or March in well-tilled land at the rate of about 14 kilos of seed per hectare. After three months the flowering stage is reached, the plants, which then contain the maximum of colouring-matter, being cut off close to the ground, tied in bundles, and despatched immediately to the factory to be extracted. A second cutting in September gives a smaller quantity of indigo.

The cultivation of indigo reached its greatest extent in 1896–1897 with a total area of 640,000 hectares, one-third in Bengal, one-fourth in the North-West Provinces, one-fourth in Madras, and one-twelfth in the Punjab. In 1880 India contained 2800 indigo factories and 6000 works employing primitive methods of extraction, the total number of persons employed, exclusive of agricultural labourers, being 360,000. After the appearance of artificial indigo, the area under indigo steadily diminished, being only 180,000 hectares in 1906–1907.

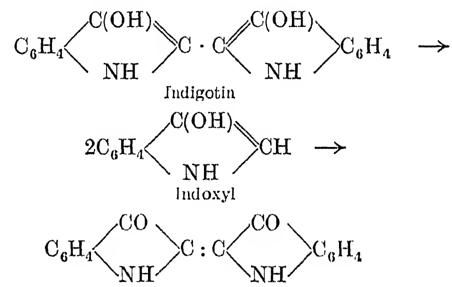
There is a tendency in India to extend the cultivation only on the most suitable soils, and to abandon the old varieties of plant in favour of Natal indigo, which gives a greater yield of leaves containing a higher proportion of colouring matter. Rational methods of extraction are also being introduced.

was extracted also in Europe (Hungary, Thuringia, etc.) from *woad* (*Isatis tinctoria*, Fig. 468), where, however, it occurs only in the leaves and in smaller quantity. There are several varieties of *Indigofera* (tinctoria, disperma, anil, argentea, and others of less importance). They are herbaceous shrubs 50 to 100 cm. in height, covered with silky hairs, with pinnate leaves and many small leaves.

From the results of tests made at Calcutta it would seem that *Indigofera leptostachya*, cultivated in Java but indigenous to Natal, is better in every respect than *Indigofera tinctoria*, while it lasts four to five years. Still better results seem to be given by *Indigofera erecta*.

In order that the indigo may be extracted from the cut plants, it is necessary that the glucoside they contain (*indican*)—consisting of a compound of glucose with indoxyl—be decomposed by fermentation in large vessels with water. After 10 to 14 hours the glucose is fermented, while the indigo, owing to the presence of ammonia, forms a yellowish solution. The liquid is transferred to deep vats, where it is subjected to " beating " for two to three hours with wooden paddles or wheels, or to " blowing " by means of a current of air. The oxidation thus effected causes the separation of the indigo in flocks, which are removed by decantation after three to four hours:

Fig. 468.



Indigotin → Indoxyl → Indigo blue

The 5 per cent. indigo paste separated by decantation is passed through sieves to remove fragments of the plants and is then boiled by means of steam for 15 minutes in order to sterilise the mass—which would otherwise undergo change—and to eliminate part of the brown matter and to effect better separation of the particles of indigo. These then deposit more easily and are collected on a large cloth filter, the first liquid passing through being returned to the filter until it comes through faint red; the 8 to 12 per cent. paste thus obtained is pressed in primitive presses. The large cakes thus formed contain about 80 per cent. of water and are cut into small cubes, which are arranged on grids, dried in the air for two or three months and placed on the market in boxes holding 50 to 140 kilos under the name of *cakes*. During the drying, these cakes evolve ammonia and become covered with mould, which is finally removed with brushes. The yield of indigo is about 0·2 per cent. on the weight of the green plant or 2 per cent. on that of the dry plant.

To combat the competition of artificial indigo, various improvements have been introduced during recent years into the methods of cultivation, manuring, and extraction; attention may be directed to the rational fermentation with suitable enzymes (oxydases) proposed by Calmette and others (Fr. Pats. 300,826 and 302,169).

The indigo-content of the cakes varies considerably, some of those on the market containing only 20 per cent. and others as much as 90 per cent. It hence becomes necessary to determine the value of any sample on the basis of the proportion of pure indigo ascertained by exact analysis.[1] According to Fr. Pat. 323,036 an increased yield and an improved

[1] **Analysis of Commercial Indigo.** Commercial indigo from Bengal contains, on an average, 60 per cent. of indigotin; that of Madras, 30 to 50 per cent.; that of Java, 72 to 82 per cent.; that of Guatemala, about 40 per cent.; that of Martinique, 60 to 70 per cent.; and that of Cambay, China, and Tonkin, 8 to 15 per cent.

Indigotin may be estimated as follows: 1 grm. of well-dried indigo is mixed (in a bottle

product are obtained by macerating the fresh plants in presence of tannin materials which leave only the indigo undissolved.

The cakes of indigo are blackish blue in colour and give a fracture showing a bronzy reflection. Natural indigo always contains, besides indigotin, other substances and colouring-matters (such as indigo gum, indigo brown and red, etc.) which affect the tint, sometimes favourably.

A good Bengal indigo gave, on analysis, 62 per cent. of indigo blue, 7·3 per cent. of indigo red, 4·7 per cent. of indigo brown, 1·5 per cent. of indigo gum, 6 per cent. of water and 19 per cent. of mineral matter.

Pure or refined indigo is obtained in various ways, *e.g.*, the crude indigo is treated with a mixture of concentrated acetic and sulphuric acids, the indigo alone passing into solution as sulphate, which is decomposed after filtration by excess of water, this precipitating pure indigo or indigotin. In order to avoid dilution with water and loss of acid, it has been proposed to separate the sulphuric acid directly by addition of calcined sodium sulphate which transforms it into bisulphate; the acetic acid is then distilled off and the bisulphate removed together with a little water. According to Ger. Pat. 134,139 pure indigo is extracted from the crude product by means of hot, crude pyridine. To purify artificial indigo, it is heated, according to Ger. Pat. 179,351, at 200° to 270°, at which temperature it does not sublime or decompose, while the indigo red and other impurities are destroyed, leaving an indigo highly valued for its fine bronzing.

Of some interest is *colloidal indigo*, which behaves like dissolved indigo, and has been recently prepared by Möhlau by heating, out of contact with the air, a suspension of indigo in an aqueous solution of alkali and sodium hydrosulphite, the liquid being treated, after cooling, with *protalbinic acid* (obtained by Möhlau by the alkaline hydrolysis of protein and subsequent dialysis; this acid has the power of precipitating various metals in a colloidal state from their salts). Addition of hydrogen peroxide to the filtered liquid gives indigo blue in the colloidal condition, which is retained even after evaporation.

PROPERTIES. Pure indigo forms a dark blue powder which, when rubbed, gives a metallic, coppery reflection. It sublimes at about 300°, giving red vapour and forming copper-red, shining prisms. It is insoluble in water, alcohol, ether, alkali, or acid, and dissolves only slightly, even in the hot, in amyl alcohol, chloroform, phenol, carbon disulphide, pure acetic acid, nitrobenzene, aniline or melted paraffin wax. It has neither odour nor taste and is indeed an almost completely indifferent substance; this explains why, although materials have been dyed from time immemorial in the Far East, in Europe no process for dyeing textile fibres was discovered for so many centuries—until the sixteenth.

The portion soluble in hot aniline colours this blue but colours fused paraffin

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with a ground stopper) with 10 grms. of garnets or glass beads and 20 c.c. of sulphuric acid mixture (composed of 3 parts of concentrated sulphuric acid and 1 part of *oleum* containing 20 per cent. of free SO_3). The mass is thoroughly mixed and is afterwards shaken occasionally over a period of 12 hours or so, until solution is complete, the whole being then poured carefully into cold water and the bottle thoroughly rinsed out. The aqueous solution is boiled for 10 minutes and filtered, the filter being washed with hot water until the washings become colourless and the filtrate then made up to a litre. Fifty cubic centimetres of this solution is mixed with 900 c.c. of distilled water, and the liquid titrated with 0·05 per cent. potassium permanganate solution until the blue colour becomes golden yellow without green reflection. In order to accustom the eye to this end-point, which is not sharp, it is advisable to make a comparative test with pure indigo of known strength; 1 c.c. of the permanganate solution corresponds with about 0·00125 grm. of indigotin. In order to prepare pure 100 per cent. indigo for purposes of comparison, 10 grms. of pure, powdered artificial indigo (98 per cent., marked B.A.S.F. or M.L.B.) is treated in a beaker with 120 grms. of caustic soda solution (sp. gr. 1·21), 330 grms. of concentrated sodium hydrosulphite solution and 100 grms. of water (or, if 50 grms. of 20 per cent. indigo paste is taken, only 60 grms. of water are added), the mixture being heated on a water-bath at 40° to 50° with occasional shaking and the air being gradually expelled from the beaker by means of a current of coal-gas. When solution is complete, the liquid is rapidly filtered and a current of air passed into the yellow or greenish filtrate. The precipitated indigo is collected on a hardened filter and washed first with hot water, then with hot dilute hydrochloric acid (30 c.c. of the concentrated acid diluted to a litre), next with water again, and repeatedly with alcohol and with alcohol and ether. When dried at 101° to 110° until of constant weight, the product represents pure 100 per cent. indigo.

wax purple-red; from these solutions, rhombic crystals showing marked dichroism separate on cooling.

From hot oil of turpentine indigo crystallises in blue plates.

Concentrated sulphuric acid converts it in the hot into a monosulphonic derivative, soluble in water but insoluble in salt solutions. With fuming sulphuric acid it forms the disulphonic compound, which gives more soluble salts, the sodium salt being sold as a paste under the name of *indigo-carmine*, this dyeing wool like an acid aniline dye.

When dry distilled, indigo gives aniline and other aromatic compounds. Energetic oxidising agents (nitric or chromic acid or permanganate) decolorise it more or less rapidly, converting it into isatin. Chlorine, bromine, and iodine give halogenated derivatives of isatin.

Indigotin white, which is the leuco-base of indigo blue, is obtained from the latter in a soluble form, by the action of alkaline reducing agents (sodium amalgam, ferrous sulphate, hypophosphorous or hydrosulphurous acid, glucose, gallic acid, etc.) or enzymes. When heated with acid, the greenish yellow alkaline solution deposits indigotin white, which is readily converted into the blue form by the oxygen of the air.

Indigo may be regarded as a substantive dye which colours both animal and vegetable fibres without a mordant. It is first reduced in the vats by means of enzymes in presence of sugar, urine, zinc, arsenic, or reducing salts (sulphites, hydrosulphites), thus becoming decolorised, soluble in alkali and capable of impregnating textile fibres, on which it becomes firmly fixed when rendered insoluble by the action of atmospheric oxygen.

In 1890 the German Government permitted alizarin blue to be used for dyeing part of the cloth for military uniforms, these having been previously coloured exclusively with indigo.

The first efforts to ascertain the chemical nature of indigo were those of Erdmann and of Laurent, who simultaneously (in 1840) obtained isatin by oxidising indigo with nitric acid. In 1848 Fritzsche obtained aniline by distilling indigo with caustic potash; Baeyer and Knop, in 1865, reduced indigo to dioxyindole, oxindole, and indole, the last of these being prepared synthetically by Baeyer and Emmerling in 1869 from *o*-nitro-cinnamic acid. In 1870 Engler and Emmerling effected the first complete synthesis of indigo by heating *o*-nitroacetophenone with lime and zinc dust, and in 1874 Nencki prepared indigo by oxidising indole and ozone.

In an interesting series of studies extending from 1870 to 1878 Baeyer and his pupils established the constitution of, and synthesised, *oxindole*, transforming it into isatin, and the latter, in various ways, into indigo. The new complete synthesis effected by Baeyer in 1880–1882 firmly established the structure of the indigo molecule.

Of the new syntheses of indigo following that of Baeyer—which, in spite of costly attempts, could not be rendered capable of industrial application—the most important from a practical point of view is that of Heumann (1890), in which fusion of phenylglycine-*o*-carboxylic acid with alkali is succeeded by oxidation.

I. The starting-point and the various intermediate products of Baeyer's 1880 synthesis of indigo are as follow:

$$C_6H_4{<}\begin{matrix}CH_2\cdot CO_2H\\ NO_2\end{matrix} \rightarrow C_6H_4{<}\begin{matrix}CH_2\\ NH\end{matrix}{>}CO \rightarrow C_6H_4{<}\begin{matrix}C(:NOH)\\ -NH-\end{matrix}{>}CO \rightarrow$$

o-Nitrophenylacetic acid — Oxindole — Isatoxime

$$C_6H_4{<}\begin{matrix}CH(NH_2)\\ -NH-\end{matrix}{>}CO \rightarrow C_6H_4{<}\begin{matrix}CO\\ NH\end{matrix}{>}CO \rightarrow C_6H_4{<}\begin{matrix}CO\\ NH\end{matrix}{>}CCl_2 \rightarrow$$

Amino-oxindole — Isatin — Isatin chloride

$$C_6H_4{<}\begin{matrix}CO\\ NH\end{matrix}{>}C:C{<}\begin{matrix}CO\\ NH\end{matrix}{>}C_6H_4$$

Indigo

Baeyer's other synthesis, which was tried on an industrial scale by the Badische Anilin- und Soda-Fabrik of Ludwigshafen in 1882, and gave a yield of 60 per cent., started from

benzaldehyde, the product of the interaction of benzylidene chloride and sodium acetate being nitrated (and subsequently esterified) and a mixture of 70 per cent. of *o*-nitrocinnamic acid and 30 per cent. of *p*-nitrocinnamic acid thus obtained. After removal of the latter, the former is converted into the dibromide, which, with alcoholic potash, loses 2HBr and forms *o*-nitrophenylpropiolic acid, this giving indigo when heated with alkali and glucose

$$\underset{o\text{-Nitrocinnamic acid}}{C_6H_4<\genfrac{}{}{0pt}{}{CH:CH\cdot CO_2H}{NO_2}} \rightarrow \underset{o\text{-Nitrophenylpropiolic acid}}{C_6H_4<\genfrac{}{}{0pt}{}{C\,\vdots\,C\cdot CO_2H}{NO_2}} \rightarrow \underset{\text{Indigo}}{C_6H_4<\genfrac{}{}{0pt}{}{CO}{NH}>C:C<\genfrac{}{}{0pt}{}{CO}{NH}>C_6H_4}$$

Owing to the high price of *o*-nitrophenylpropiolic acid, this artificial indigo is used only for printing textiles.

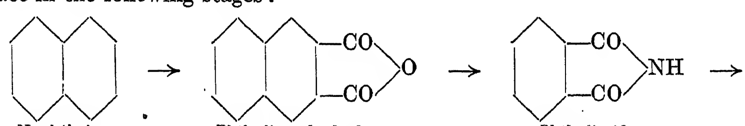
II. In 1882, by means of a new and theoretically elegant synthesis, Baeyer and Drewson succeeded in raising the yield to 70 per cent.; *o*-nitrobenzaldehyde and acetone were condensed in presence of caustic soda, indigo being formed as follows:

$$\underset{o\text{-Nitrobenzaldehyde}}{2C_6H_4<\genfrac{}{}{0pt}{}{CHO}{NO_2}} + \underset{\text{Acetone}}{2CH_3\cdot CO\cdot CH_3} = 2C_6H_4<\genfrac{}{}{0pt}{}{CH(OH)\cdot CH_2\cdot CO\cdot CH_3}{NO_2} =$$

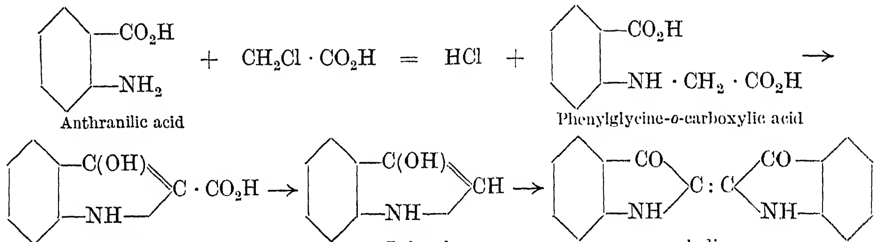
$$2H_2O + 2CH_3\cdot CO_2H + \underset{\text{Indigo}}{C_6H_4<\genfrac{}{}{0pt}{}{CO}{NH}>C:C<\genfrac{}{}{0pt}{}{CO}{NH}>C_6H_4}$$

In printing, the synthesis takes place directly on the fabric, the acetone being rendered soluble by conversion into the bisulphite compound (*Kalle's salt*). The industrial preparation of *o*-nitrobenzaldehyde presented, however, a serious disadvantage, the direct nitration of benzaldehyde yielding a considerable proportion of the unusable *m*-nitrobenzaldehyde: whilst, starting from benzil, the *p*-nitro-compound is obtained. A happy solution of this difficulty was found in the preparation of *o*-nitrotoluene directly from toluene (only 40 per cent. of *p*-nitrotoluene is formed), oxidation with manganese dioxide and sulphuric acid then giving a good yield of *o*-nitrobenzaldehyde. To the general application of this process were opposed a number of difficulties. In order that the artificial indigo might displace the natural product, the annual consumption of which was about 5,000,000 to 6,000,000 of kilos (100 per cent.), it was necessary that there should be on the market a sufficient quantity of raw material (toluene) at a reasonable price. It was found that, even although the use of modern metallurgical coke furnaces (*see* Vol. I., p. 451, and this Vol., p. 632) increased the quantity of crude benzene (in 1900 the total output in Europe amounted to 30,000 tons), yet, since the latter contains only one-sixth of its weight of toluene and since 4 kilos of toluene are required to furnish 1 kilo of artificial indigo, the use of all the toluene extractable from the benzene on the market would give only 1,000,000 kilos of indigo, *i.e.*, one-fifth or one-sixth of the whole consumption. Increase of the production of crude benzene for the purpose of obtaining more toluene would lead to over-production of unusable benzene, and hence to increase in the price of toluene and in that of artificial indigo, which would be unable to compete with the natural product.

III. After much further investigation and many unsuccessful trials, the industrial preparation of artificial indigo has, however, become an accomplished fact. Having acquired Baeyer's patents for a sum approaching £20,000 without deriving any practical benefit from them, the Badische Anilin- und Soda-Fabrik of Ludwigshafen did not hesitate to purchase later the patents of K. Heumann, who was the first to discover, in 1890, that indigo is obtained on fusion of phenylglycocoll with caustic potash, but that a better yield is obtained if the phenylglycocoll is replaced by phenylglycine-*o*-carboxylic acid, $C_6H_4(CO_2H)(NH\cdot CH_2\cdot CO_2H)$. The economical preparation of this acid necessitated investigations and trials extending over more than seven years, and the synthesis became of industrial value only when it was found possible to employ naphthalene as the initial substance. Quite 50,000 tons of naphthalene are produced annually in the distillation of tar, and up to that time only about 15,000 tons of this had been utilised, the rest being left in the heavy tar-oils or used for making lamp-black (p. 624). The complete synthesis takes place in the following stages:



Naphthalene Phthalic anhydride Phthalimide



Anthranilic acid — Phenylglycine-*o*-carboxylic acid

Indoxylic acid — Indoxyl — Indigo

The oxidation of naphthalene to phthalic anhydride by means of chromic acid is too expensive, but the same end was attained by the use of fuming sulphuric acid rich in sulphur trioxide, after it had become possible to prepare this cheaply by the catalytic method (*see* Vol. I.). The action of the acid was moderated with mercury bisulphate, while the sulphur dioxide was recovered by the catalytic process (in 1901 the Badische Company recovered in this way, for the manufacture of phthalic anhydride alone, about 40,000 tons of sulphur dioxide).

Phthalimide is then easily obtained by the action of ammonia, while the monochloroacetic acid can be prepared cheaply and in large quantity by using the liquid chlorine (1,000,000 kilos in 1900) resulting from the electrolytic manufacture of caustic soda or potash, and glacial acetic acid (about 20,000 quintals) obtained from the distillation of wood (about 100,000 cu. metres per annum). The reaction between anthranilic acid and monochloroacetic acid proceeds readily, but the formation of indoxylic acid was found to be much more difficult, the conditions required for the fusion of the phenylglycinecarboxylic acid being inconvenient; this obstacle was, however, finally overcome. The ultimate oxidation of the indoxyl is effected by means of a current of air. The indigo separates in small crystals, and in order to obtain it in a finely divided state, it is converted into sulphate and this decomposed with water. After being washed, the paste thus formed is identical with natural indigo and is, indeed, of greater value owing to its higher purity and to its constancy of composition.

IV. *Process of the Farbwerke vormals Meister, Lucius und Brüning of Höchst* (1900). This consists in the action of sodamide (obtained by treating gaseous ammonia with sodium) on phenylglycocoll, subsequently heating in an autoclave at 250°:

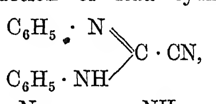
$$NH_2Na + C_6H_5 \cdot NH \cdot CH_2 \cdot CO_2Na = NH_3 + Na_2O + C_6H_4{<}^{CO}_{NH}{>}CH_2 \text{ (indoxyl)},$$

2 mols. of the indoxyl then condensing in presence of oxygen:

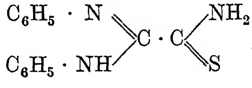
$$2C_6H_4{<}^{CO}_{NH}{>}CH_2 + O_2 = 2H_2O + C_6H_4{<}^{CO}_{NH}{>}C : C{<}^{CO}_{NH}{>}C_6H_4.$$

This process was originally patented by the Deutsche Gold- und Silber-Scheide Anstalt (Frankfort), from whom it was purchased. A yield as high as 65 per cent. has been obtained, but sodium at 28*d.* per kilo is too expensive to make the process practicable.

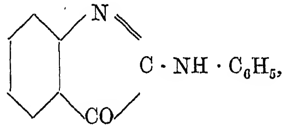
V. *Sandmeyer's synthesis* (patented by Messrs. Geigy of Basle; Eng. Pat. 15,497 of 1899). Aniline is treated with carbon disulphide in presence of alcoholic potash, diphenylthiourea being obtained: $CS_2 + KOH + 2C_6H_5 \cdot NH_2 = KHS + CS(NH \cdot C_6H_5)_2 + H_2O$. The action of lead cyanide on diphenylthiourea gives **Hydrocyanocarbodiphenylimide**,



which with ammonium sulphide yields the **Thioamide**,



, and this with sulphuric acid forms **α-Isatinanilide**,



reduction of the latter by means of ammonium sulphide then giving indigo. All the materials used in this synthesis are cheap, but the indigo produced was not able to compete for long

with that of the Badische Company and of Messrs. Meister, Lucius und Brüning, who continually lowered the price in order to suppress natural indigo and made use of the two improved Heumann processes starting from phenylglycocoll and phenylglycinecarboxylic acid.

The struggle, lasting for more than twenty years, between the producers of natural indigo and the scientific men connected with the various industrial undertakings has now ended in uncontested victory for the latter. The figures already given showing the areas under indigo at different times (*see* p. 759) justify the conviction that in a few years' time *Indigofera tinctoria* will be of interest only historically, just as is the case with madder, now supplanted by artificial alizarin.

With its lower price, its more ready applicability in dyeing, and the considerable use now made of its halogenated derivatives, the consumption of indigo will certainly increase. In 1908, owing to the slight difficulty of reducing indigo, even when finely powdered, several firms placed on the market the leuco-product itself (indigo white), this being obtained by reduction with iron and alkali, or, better, with hydrosulphite (*Grandmougin*), etc.

The following figures will give a clearer idea of the commercial and industrial importance of indigo, both natural and artificial.

STATISTICS. The production in India was 50,000 quintals in 1892 and 75,000 quintals (containing 56 to 70 per cent. of indigotin), of the value of £3,200,000, in 1896. Of Indian indigo 60 per cent. is sold at Calcutta, which supplies Europe and America, 30 per cent. at Madras to Egypt and the East, and 10 per cent. at Bombay and Karachi.[1]

The output of indigo (with 56 to 70 per cent. of indigotin) and the surface under cultivation in India were as follows:

	1892	1896	1909	1912	1913	1917	1918–19	1919–20	1920–21
Quintals	50,000	75,000	12,000	23,850	18,800	48,000	22,000	19,000	24,000
Hectares	—	640,000	150,000	86,000	80,000	170,000	120,000	95,000	73,000

In 1895 the consumption of indigo in different countries was as follows: England, 13,000 quintals; United States, 11,500; Germany, 10,000; France, 7100; Belgium, 1500; Austria-Hungary, 5500. In 1913 the world's consumption of indigo (calculated for 100 per cent.) was estimated to be 100,000 quintals, the price being lowered by the competition of new vat dyestuffs (indanthrene, etc.) which compare favourably with indigo as regards fastness and price.

The *price* of indigo (100 per cent.) was 16*s.* per kilo between 1895 and 1900, 12*s.* in 1902 and 6*s.* 6*d.* in 1904, the fall being due partly to competition between the two great firms, the Badische Anilin- und Soda-Fabrik, and Messrs. Meister, Lucius und Brüning, who later came to an agreement, the price then rising to 8*s.* per kilo. In 1917 the price was more than quintupled, and in 1921 it fell to about double the pre-war value.

In 1907 the total output of artificial indigo was estimated at about 4320 tons (100 per cent.), *i.e.*, about four-fifths of the world's consumption.[2]

[1] In 1882 the Indian Government abolished the export duty on indigo. Until 1865 almost all the indigo was sent to London, which was the centre of the European trade. In 1905–1906 exportation from India had fallen to 15,000 quintals (£400,000), the cultivation of indigo being replaced by that of *rubber* (28,000 quintals), *turmeric* (25,000 quintals), hemp, cotton, tanning plants, etc. During recent years the cultivation of natural indigo has increased in the districts more suitable to it and diminished in those less fitted.

In 1866 the Philippines exported 251,574 kilos of indigo paste (£96,950) and 959,206 kilos of liquid indigo (*tintarron*) (£28,180). The industry was still flourishing in 1875–1881, when the producers began to adulterate with sand and other substances; prices were thus ruined and fell from £12 per quintal to £4, the cultivation being to some extent abandoned. With careful cultivation, as much as 4 quintals of good indigo can be obtained per hectare. By 1905 the exportation had diminished to a total of 250,000 kilos of pasty and liquid indigo. The output in Java amounted to 500,000 kilos in 1905, but in 1909 the exports were only 100,000 kilos.

The increasing competition of artificial indigo led to the formation, in 1920, of the Indigo Planters' Co-operative Association, supported by about one-half of the countries producing indigo, with the objects of centralising the treatment, placing on the market a uniform grade of indigo free from adulteration, and improving the methods of cultivation, since much land used for growing indigo had become almost sterile. It has been found that suitable artificial fertilisation, especially with superphosphates, raises the yield to 45 kilos per hectare. The fermentation of indigo was formerly carried out in cement tanks and was retarded by the lime liberated by hydrolysis of the cement.

It appears that natural indigo, properly prepared, gives results about 10 per cent. better than those yielded by the artificial product having the same indigotin content.

[2] The first artificial indigo plant of the Badische Anilin- und Soda-Fabrik in 1897 cost

CC. COLOURING-MATTERS

Only a certain proportion of the innumerable *coloured substances* are capable of being fixed on vegetable or animal fibres, imparting to them a more or less stable coloration, and only those able to fulfil this function, directly or indirectly, belong to the true Colouring-Matters.

Coloured substances are those which absorb constituents of white light of certain definite wave-lengths, emitting the rest.

Generally speaking, only the luminous waves visible to the eye have yet been closely studied, and it is probable that new laws, possibly more important than those already known, will be discovered when the infra-red and ultra-violet rays absorbed or reflected by coloured substances are considered.

Hartley has indeed shown that the apparently colourless substance, benzene, is, strictly speaking, coloured, as it absorbs certain ultra-violet rays invisible to the eye, and that in the benzene series the luminous vibrations are gradually rendered slower and so made visible as the molecular weight is increased by substituent groups.

Dichroic Substances allow certain rays to traverse them and reflect certain others, so that they appear to be of one colour by transmitted, and of another by reflected, light; such are, for example, fluorescent substances. Certain alkaline fluorides, such as those of the alkali metals, allow infra-red and ultra-violet radiations to pass through them, while various nitrates, nitric acid, the hydrocarbons, the aldehydes, etc., although they do not retain any of the constituents of white light and hence appear colourless, yet do absorb waves of many wave-lengths.

Light itself is to the human organism only a sensation due to absorption of a portion of the radiations by the crystalline lens of the eye.

Between coloured and non-coloured substances there is often complete or nearly complete identity in chemical *composition*, so that the colour depends, not on the composition, but only on the *constitution* or atomic structure of the molecule.

It is now universally admitted that the colour of substances is closely dependent on the presence in the molecule of certain well-defined atomic groupings or nuclei.

As early as 1867 Graebe and Liebermann arrived at the conclusion that the colouring-matters capable of fixing hydrogen with decoloration and formation of the so-called *leuco-bases* (*see* p. 721) are transformed into colouring substances on oxidation.

In 1876 N. O. Witt defined the nature of these *simple groups*, termed *chromophores* (*e.g.*, $-NO_2$, $-N:N-$, $=CO$, $=NH$, $\equiv C \cdot NO$, $=C=S$, $=C:C=$, $-N:N-$, etc.), which by union with more complex groups (even colourless ones like the aromatic hydrocarbons, benzene, naphthalene, etc.) form the so-called *chromogens*, these being usually more or less coloured, but not colouring. Thus, azobenzene, $C_6H_5 \cdot N:N \cdot C_6H_5$, is a chromogen containing the chromophore, $-N:N-$, and is coloured red, but does not dye textile fibres, although it is the mother substance of dyestuffs. Repetition of one and the same chromophore in a chromogen may alter the colour, *e.g.*, from yellow to green, blue, etc. (such chromophores are called hypsochromic), or from yellow to orange, red, etc. (bathochromic).

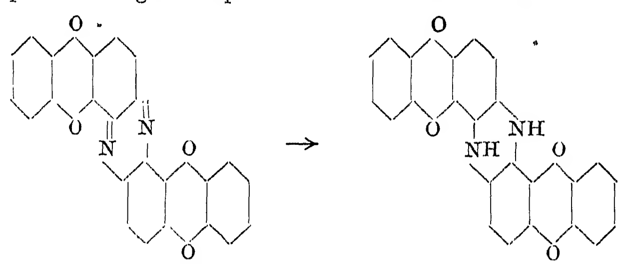
£480,000, and in 1900 two competitors, namely, Messrs. Meister, Lucius und Brüning and Messrs. Geigy, made their appearance, the considerable fall in price thus produced resulting in Messrs. Geigy's abandonment of the manufacture and of the fusion of the indigo interests of the two remaining firms with a capital of £1,200,000. In 1910 the manufacture of artificial indigo was started by the Rahtjen Company of Hamburg—which is a company with a capital of £280,000 and makes use of Rahtjen's improved Sandmeyer process—and by the firm of Heyden (Radebeuf) which employs the phenylglycine method. The Society of Chemical Industry in Basle also began making artificial indigo in 1911–1912. During the war the manufacture was commenced in England, the United States, and France.

Coloured chromogens usually become colourless by fixation of hydrogen; thus, $C_6H_5 \cdot N : N \cdot C_6H_5$ (azobenzene, orange) $+ H_2 = C_6H_5 \cdot NH \cdot NH \cdot C_6H_5$ (hydrazobenzene, colourless); $C_6H_4O_2$ (benzoquinone, yellow) $+ H_2 = C_6H_6O_2$ (quinol, colourless). The original coloured compound is obtained on oxidation of the colourless compound, which is known as a *leuco-derivative*. Dibiphenylenethene, $\begin{matrix}C_6H_4\\ | \\ C_6H_4\end{matrix}\!\!>C = C<\!\!\begin{matrix}C_6H_4\\ | \\ C_6H_4\end{matrix}$, a red hydrocarbon, gives the colourless dibiphenylenethane, $\begin{matrix}C_6H_4\\ | \\ C_6H_4\end{matrix}\!\!>CH \cdot CH<\!\!\begin{matrix}C_6H_4\\ | \\ C_6H_4\end{matrix}$, on reduction.[1]

CHROMOGENS are numerous and of very varied composition.[2]

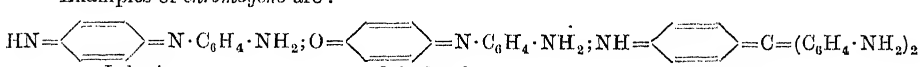
[1] Some of these leuco-products regenerate the original colouring-matter simply by oxidation, while others do not. For instance, reduction of nitro-groups gives, as final products, amino-derivatives, which yield nitro-groups again on oxidation. The complete reduction of azo-compounds yields amino-groups, but there may also be intermediate, less highly reduced products (hydrazo-compounds), which are themselves new *leuco-derivatives*.

In some cases reduction leads to more highly coloured substances. For instance, the greenish-yellow anthraquinoneazine gives deep blue indanthrene on reduction:

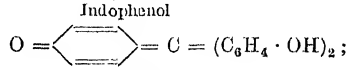


the two imino-groups formed being intense auxochromes, especially if they occur in a closed ring. Similarly indigo with the auxochrome, $—CO—C = C—CO—$, should be yellow, but is blue owing to the presence of two auxochromes forming closed rings.

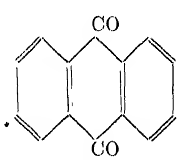
[2] Examples of *chromogens* are:



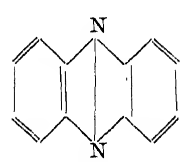
Indamine Indophenol Rosaniline



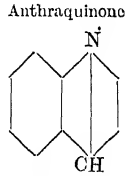
Rosolic acid



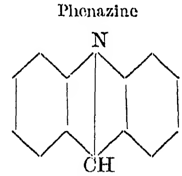
Anthraquinone



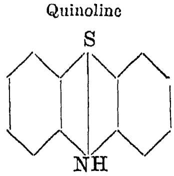
Phenazine



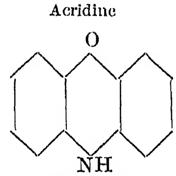
Quinoline



Acridine



Thiodiphenylamine



Phenoxazine

Introduction of amino groups into the chromogen azobenzene is accompanied by a deepening of the colour from yellow to orange to brown, these chromophores being bathychromic :

Aminoazobenzene, $C_{12}H_9N_2 \cdot NH_2$, is pale yellow.

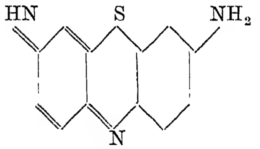
Diaminoazobenzene, $C_{12}H_8N_2(NH_2)_2$, is orange.

Triaminoazobenzene, $C_{12}H_7N_2(NH_2)_3$, is brown.

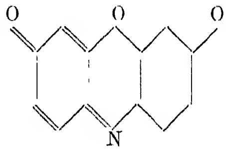
Chromogens are mostly neutral substances and if groups—termed auxochromes—capable of imparting a basic or acid character are introduced, colouring matters capable of dyeing textile fibres are obtained. The auxochromes are, more especially, hydroxyl and amino groups and their alkyl or phenyl derivatives : OH, NH_2, OCH_3, $NHCH_3$, $N(CH_3)_2$, NHC_6H_5, $N(C_6H_5)_2$. Hydroxylamine and hydrazine residues, $NH \cdot OH$ and $NH \cdot NH_2$, may also behave as auxochromes, but the auxochromic character diminishes or disappears on entry of an acid substituent, as in $O \cdot COCH_3$, $NH \cdot COCH_3$, $N(CH_3) \cdot NO$, etc. Sometimes the auxochrome group is formed during the dyeing, as when the group $= CO$ becomes $\equiv C \cdot OH$.[1]

Further, what are usually the more energetic chromophores cease to be so when they occur in molecules which are small or poor in carbon. To this is due the very small number of colouring-matters in the aliphatic series.

Thirteen chromophores of well-defined constitution are now known, while concerning others there is still doubt owing to the pseudoisomerism (tautomerism) they exhibit.[2]



Thionine



Resorufin

In these chromogens is seen the analogy between the chromophores in the different molecules, characterised by divalent or polyvalent atoms or atomic groups ($= NH$, $= N—$, C O, S, —O—, $>CO$) united to the ring in a closed chain, the whole forming the true chromophore, which, joined to the rest of the molecule, gives the chromogen.

The passage from simple to more complex chromophores is often accompanied by change from a yellow colour to a more intense yellow or to red or blue.

[1] With fuchsines (rosanilines and *p*-rosanilines) the colour becomes more intense and more violet with increase in the alkyl groups replacing the aminic hydrogen. The faintly acid, phenolic colouring-matters which are fixed by mordants give highly resistant colours if they contain at least two OH groups, or OH and COOH, in the *ortho*-position, and better still if these are also in ortho-positions with respect to the chromophores. In the colouring-matters of the nitrophenol group, the colour passes from greenish yellow to orange-yellow as the distance between the OH and NO_2 groups increases. Fast colours on mordants are given especially by those colouring-matters containing hydroxyl-groups in the ortho-position with respect to one another and to the chromophore (alizarin, etc.).

Of the triphenylmethane colouring-matters, those which have a sulphonic group (SO_3H) in the ortho-position with respect to the central carbon atom are stable to alkali and to soap (Suais and Sandmeyer).

[2] According to Hantzsch (1906) all the true nitro-hydrocarbons of the aromatic or aliphatic series and also all polynitro-compounds are colourless when quite pure, so that the NO_2 group by itself is never a chromophore. Only certain nitrophenols are coloured when their phenolic hydrogen is free and hence mobile (forming tautomeric compounds), and for the same reason all salts of nitrophenols are coloured. By the discovery of the quinonic (aci-) ethers of nitrophenols besides the true ethers, it was shown that many colourless or almost colourless hydrogenated compounds capable of forming highly hydrogenated salts, are pseudo-acids, so that the coloured salts are derived from a hydrogenated compound differing from the original ; if it were possible to obtain these free, they also would be coloured.

Nitrophenols are certainly true tautomeric hydrogenated compounds which give two series of structurally isomeric ethers, such as are given also by nitrous, sulphurous, hydrocyanic, and cyanic acids. The true nitrophenolic ethers are colourless, while the aci-ethers (tautomeric) are coloured an intense red ; the former correspond with the general formula, $C_6H_4\left\langle{}^{O \cdot C_nH_{2n+1}}_{NO_2}\right.$ (derived from the colourless true nitrophenol, $C_6H_4\left\langle{}^{OH}_{NO_2}\right.$), and the latter

Certain acid groups (CO_3H, CO_2H, etc.), *i.e.*, *salt-forming groups*, influence the colour but, even more than the chromophores, reinforce the influence of the auxochromes. Thus, azobenzene, $C_6H_5 \cdot N : N \cdot C_6H_5$, although a coloured

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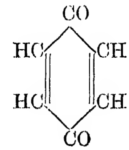
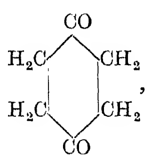
with $C_6H_4\left\langle\begin{matrix} O \\ NO \cdot OC_nH_{2n+1} \end{matrix}\right.$ [derivatives of aci-nitrophenol (quinonic), $C_6H_4\left\langle\begin{matrix} O \\ NO \cdot OH \end{matrix}\right.$]. It is hence possible to tell, from the mere colour, to which of the two groups a given nitro-compound belongs. When true nitrophenols (even in the solid state) are slightly coloured, it is assumed that a minimum quantity of the aci-nitrophenol is dissolved in a large quantity of true nitrophenol (solid solution). Also, the fact that the colour of the substance is sometimes not intensified by increase in the number of nitro-groups is explainable, not on the old view of the theory of chromophores, but only by the new *theory of transposition* (tautomerism):

$$C_6H_4\left\langle\begin{matrix} OH \\ NO_2 \end{matrix}\right. \rightleftarrows C_6H_4\left\langle\begin{matrix} O \\ NO \cdot OH \end{matrix}\right.$$

The tendency to tautomeric transposition may, indeed, be increased or diminished by the entry of new groups. Thus, in solutions of nitrophenols and their salts, the coloration is not—as it would be according to the modern theory of indicators (*see* Vol. I., p. 100)—due to ionisation, but rather to the formation of coloured tautomeric compounds (aci-nitrophenolic ethers) in agreement with the old chemical theory of indicators.

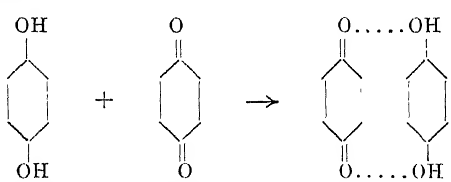
It is thus proved that the formation of coloured salts and coloured ions derived from colourless hydrogenated compounds is of a purely chemical nature. It is caused first of all by intramolecular transposition, from which, by the action of a positive metal (salt), there results a negative quinonic atomic grouping (chromophore), the appearance of coloured ions being a secondary reaction. Hence the actions of chromophore and of auxochrome cannot be held to be distinct but are exerted together, both of them (nitro- and phenol-group) causing the appearance of colour at the expense of their mutual transformation, which generates a quinonic grouping containing neither nitro- nor phenolic-group.

These views may be extended to other groups of organic substances since, in general, colourless acids unchangeable in constitution (*i.e.*, not giving tautomeric forms) give only colourless ions and yield colourless salts with colourless metallic oxides, and colourless ethers and esters with colourless organic radicals (alkyl and acyl). If coloured ions and salts are derived from a colourless alkyl compound, it may be stated with certainty that intramolecular change occurs.

According to E. Fischer and O. Fischer (1900) many colouring-matters derive their properties from the presence in the molecule of quinonoid groups, although A. v. Baeyer (1902–1905) and Hantzsch (1905) showed that the true quinone group does not always cause coloration (*i.e.*, is not the chromophore), and Kostanecki and Haller pointed out that, in addition to the two carbonyl groups of the quinone, two ethylene double linkings must be present,  ; in fact, diketohexamethylene,  , which has not these double bonds, is completely colourless.

As a metaquinone with two ethylene double linkings cannot exist, such meta-compounds are incapable of producing colouring-matters.

Further, according to Willstätter's results (1908), conversion of the benzenoid to the quinonoid form is not sufficient to produce intense coloration, since then the complete quinonoid derivatives (holoquinonoid) should be highly coloured, whereas the benzoquinones, like the quinonimines $O : C_6H_4 : NH$ and $NH : C_6H_4 : NH$, are only slightly coloured. On the other hand, quinhydrones, formed by the condensation of quinol and quinone *viâ* the partial valency, are highly coloured compounds:

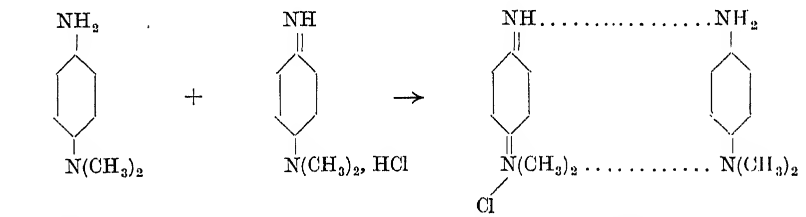


Quinol (colourless)   Quinone (yellow)   Quinhydrone (highly coloured)

chromogen (containing the chromophore $\cdot N:N\cdot$), does not colour textile fibres since it is neutral, whilst its sulphonic derivative is a feeble colouring-matter. Also the direct introduction of sulphonic groups into true colouring matters usually produces, not an intensification, but a distinct attenuation. However, these groups, which are feeble auxochromes, give to the colouring matter an acid character which influences its behaviour towards various textile fibres and thus, besides rendering certain insoluble colouring matters soluble in water, makes them suitable (either as they are or after salt-formation) for dyeing wool and silk directly in an acid bath; that is, they form the group of *acid dyestuffs*. The auxochromic function of the sulphonic group increases with its proximity to the chromophore group.

The basic auxochromes usually consist of amino groups more or less substituted by alkyl or phenyl residues, etc., and are transformed under certain conditions into chromogens, giving rise to *basic dyestuffs* which dye wool and silk directly in a neutral or slightly acid bath and dye cotton only after this has been mordanted with tannin.

When similar auxochromes and chromophores are both able to form salts, the salt-formation of the chromophore is the more important, as is shown by the behaviour of the rosanilines.[1]



Dimethyl-*p*-phenylene-diamine (colourless) — Dimethylquinonedi-imine (yellow) — Wurster's red (highly coloured)

These partially quinonoid compounds are termed *meriquinonoid*. The intense colour of magenta may be explained by the simultaneous presence of a quinonoid nucleus probably united by partial valencies to the benzenoid group or groups and, moreover, to the methane carbon atom.

With certain groups of substances intensification of the colour is due more especially to a phenomenon of *salt formation*, *e.g.*, with the rosanilines, the base of malachite green and crystal violet. Colourless phenolphthalein gives a red sodium salt, and yellow alizarin becomes intense violet in alkaline solution. In certain cases only salt formation annuls the coloration; thus the three nitroanilines are yellow, but become colourless when salified by an acid, the latter paralysing the auxochrome action of the amino group.

On salt formation aminoazobenzene gives an orange-yellow colour for the azoid form, $C_6H_5\cdot N:N\cdot C_6H_4\cdot NH_2,HCl$, and a violet colour for the quinonoid from, $C_6H_5\cdot NH\cdot N:C_6H_4:NH,HCl$.

[1] Rosaniline, $HN=C\left\langle\begin{matrix}CH-CH\\CH-CH\end{matrix}\right\rangle C=C\left\langle\begin{matrix}C_6H_3\left\{\begin{matrix}CH_3\\NH_2\end{matrix}\right.\\C_6H_4\cdot NH_2\end{matrix}\right.$ (*see corresponding base*, p. 721),

which is coloured, contains as chromophore the group $NH=C\left\langle\begin{matrix}CH=CH\\CH=CH\end{matrix}\right\rangle C\langle$, and as auxochromes two amino-groups. When the salt with a single molecule of HCl is obtained and the substance is dyed red, proof is given that the salt is formed with the imino-group of the chromophore, since a red coloration is formed on the fibres. On the other hand, salts of rosaniline with 2 or 3 molecules of HCl, which form salts also with the auxochrome amino-groups, are yellow but do not dye textile fibres yellow. It can hence be affirmed that the auxochromes do not unite with the fibres and hence have no action as salt-forming groups but only contribute to increase the basic character of the colouring-matter or even to increase the intensity of the colour; this is clearly shown with safranine (*see later and also above*, Aminoazobenzene). In general, the union of an acid chromophore with a basic auxochrome gives colouring-matters of slight intensity; for instance, the nitroanilines are feeble and the nitrophenols more intense colouring-matters.

The replacement of the hydrogen of the auxochrome OH by a metal increases the power of the auxochrome, while an alkyl or aromatic radical lowers it and an acid radical often annuls it.

If the auxochrome of a colouring-matter is weak and the chromophore strong, or *vice versâ*, the colouring-matter is generally feeble.

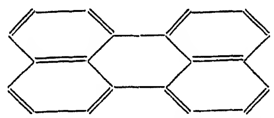
Kaufmann (1921) considers that carboxyl and sulphoxyl, $\cdot SO_2 \cdot OH$, act as auxochromes, not when they are united directly to the chromophore, but only when separated from it by either a benzene nucleus or a corresponding group.

The carboxyl group, a weak acid auxochrome, increases the fastness of the colour and often imparts the ability to form *lakes* with metallic mordants.

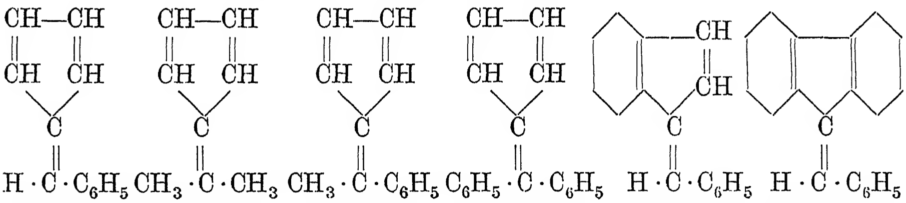
The nitro group acts as a chromophore and, when added to other chromophores, renders the colour faster and displaces it towards the blue. A similar action is shown by the halogens, but iodine is little used owing to its cost; bromine, which deepens the colour, is used for eosins and also for vat dyestuffs.

Alkyl groups, as part of the chromogen, exert little influence, but render the colour more blue and more brilliant if they occur in the auxochromes as either alkylaminic groups, as in Hofmann's violet, or alkyloxy groups. Similar behaviour is shown by arylaminic groups, NHAr, as in aniline blue and alkali blues.

Colour in an organic compound was formerly regarded as being connected with the presence in the molecule of nitrogen, oxygen or sulphur, and the colour of a few hydrocarbons was considered exceptional or due to traces of impurities. Various coloured hydrocarbons are, however, now known. Diphenylbutadiene and the two tetraphenylbutadienes, $C_6H_5 \cdot CH : CH \cdot C(C_6H_5) : C(C_6H_5)_2$ and $C(C_6H_5)_2 : C : C : C(C_6H_5)_2$, are colourless, but diphenylhexatriene and tetraphenylhexatriene, $C_6H_5 \cdot CH : CH \cdot CH : CH \cdot C(C_6H_5) : C(C_6H_5)_2$, are yellow.

Perylene, , also, is coloured.

Of more interest are the following hydrocarbons derived from fulvene:



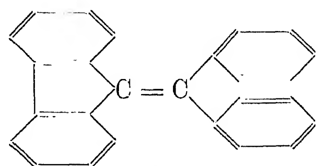
Phenylfulvene, deep red; Dimethylfulvene, orange-yellow; Phenylmethylfulvene, red; Diphenylfulvene, red; Phenylbenzofulvene, yellow; Phenyldibenzofulvene, colourless

Many coloured fulvene derivatives were prepared by Courtot (1915) by means of the Grignard reagent.

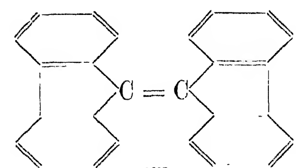
These and other similar compounds contain the *fulvenic chromophore* or, more generally, at least three conjugated double linkings, $-\underset{|}{C}=\underset{|}{C}-\underset{|}{C}=\underset{|}{C}-\underset{|}{C}=\underset{|}{C}-$ (Thiele, 1899). Of the two tetraphenylbutadienes (*see above*), however, the

Substitution of the hydrogen of the auxochrome NH_2 by alkyl radicals raises the colouring power, while two aromatic radicals sometimes lower it considerably, exceptions to this being shown by sulphonyl and picryl, $C_6H_2(NO_3)_2$, which cause the NH_2 group to assume an acid character. The *hydrazinic* and *hydroxylaminic* groups also behave as *auxochromes*; thus phenylhydrazine is slightly yellow while aniline is colourless, and nitrophenylhydrazine is more highly coloured than nitroaniline. Anthraquinone (faintly acid chromogen) gives an intensely coloured derivative with hydrazine groups. The hydroxylamine derivatives are few in number and have been but little studied. H. Kaufmann (1911) has shown that two auxochromes reinforce one another when they are in the para-position and to a less extent or not at all when they are in the ortho- or meta-position. This rule is confirmed, not only by the greater intensity of the colour, but also by the increased luminescence or fluorescence assumed by these substances when they are exposed to ultra-violet rays (*see* Vol. I., p. 125); in solution, only compounds of the para- series give direct fluorescence. By the law of distribution it is proved that the maximum and sometimes the only effect of auxochromes in the para-position is exerted when the chromophore and auxochrome are in the same benzene nucleus.

first contains only two conjugated double linkings and the second the linking $C = C = C = C$, both of these compounds being colourless; the coloured di- and tetra-phenylhexatrienes contain three conjugated double linkings. Perylene contains six such linkings and is coloured, whereas tetraphenylethylene is colourless, as the conjugated linkings are not accumulated in a restricted nucleus as in perylene. It is sufficient, however, to establish a conjugation between two double linkings of two phenylic nuclei to obtain a yellow colour, as in diphenyldibenzofulvene (I), two such conjugations, as in diphenylenedibenzofulvene (II) giving a red colour.



(I)



(II)

The fact that phenyldibenzofulvene is colourless, whilst phenylbenzofulvene, with the same number of conjugated double linkings, is coloured is explained by the presence in the latter of fewer benzene nuclei and hence of a greater accumulation of double linkings (Kaufmann, 1904).

As regards the constitution of dyestuffs benzenic double linkings must be distinguished from ethylene linkings, the latter being less saturated than the former and combining more readily with bromine and hydrogen owing to the residual partial valencies (*see* p. 620).

For dyeing purposes the colouring-matters are placed on the market in a state soluble in water, the auxochrome groups being converted where possible into salts (*e.g.*, SO_3Na, etc.). When wool (which is both basic and acid in character) is dyed with acid colours, since the basic properties of the wool are usually not sufficiently strong to displace the metal (Na) of the acid colour, an energetic acid (acetic or sulphuric) is added to the hot aqueous dyeing bath, this liberating the acid residue of the colouring-matter, which can then combine with the basic group of the wool to form a coloured stable insoluble salt in the fibre itself.

Thus wool is dyed directly both by acid and by basic colours (with the latter it is not necessary to render the bath acid). Cotton, on the other hand, is not usually dyed by acid dyes but only by basic ones, and then only when the fibres are previously mordanted with tannin materials and metallic salts.

During the past twenty years, however, numerous *neutral* or *substantive dyestuffs* have been discovered, capable of dyeing cotton directly in a neutral or faintly alkaline, but not acid, bath, previous mordanting being unnecessary. Many of these colouring-matters have a common *benzidine* group (*see* p. 718), others contain a basic group (primulin) and others again a phenolic group (curcumin). Colouring-matters sometimes acquire this property by mere accumulation of chromophores in a single molecule (Rupe, 1901). The nature of the metal present in these colouring-matters alters to some extent the properties and the affinity towards cotton, but this is always related to the capillary constant of the aqueous solution. The precipitation of the unaltered colouring-matter on the fibres is facilitated by increasing the osmotic pressure of the bath by the addition of considerable quantities of salts (NaCl or Na_2SO_4).

As a rule phenolic compounds form weak colouring-matters, but they have the property of giving intensely coloured *lakes* with metals (phenoxides), the metallic atom united to the phenolic oxygen functioning as an energetic auxochrome. These colouring-matters having no affinity for textile fibres, the latter are previously charged with metallic oxides (*mordants*). Lakes of different colours are formed with different metals (Hummel hence called such colouring-matters *polygenetic*), but for practical purposes it is indispensable that they

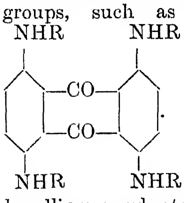
should be resistant to atmospheric agents and to ordinary physico-chemical treatment.[1] The best among these substances are those containing in the ortho-position either two phenolic groups (OH) or one OH and one COOH, and of such those are best in which these groups are in the ortho-position with respect to the chromophore (Liebermann and Kostanecki, 1887–1893) and in which the auxochrome is formed from iron, aluminium, or chromium. Not all colouring-matters which give insoluble lakes can be fixed on fibres mordanted with metallic oxides, and this perhaps depends on the fact that only certain coloured lakes are capable of combining with the fibre, the constitution of the colouring-matter (*see* Alizarin) being here also of considerable importance.[2]

When basic or neutral colouring-matters are sulphonated with concentrated H_2SO_4, *acid colouring-matters* (Simpson and Nicholson, 1862) are often obtained. In the form of soluble salts of the alkali metals, these can be fixed directly, in an acid bath, on animal fibres with the same colour as the colouring-matter, the animal fibre forming a kind of new salt; indeed the fibre assumes the colour of the original salt of the colouring-matter and never that of its free coloured acid liberated in the bath by means of acetic or sulphuric acid (*see above*, Process of Dyeing). These acid colours are fixed also by cotton, provided the latter is first rendered basic either by nitrating and then reducing, or by oxidising (oxycellulose), or by hydrating (with NaOH: mercerisation), or by treating with NH_3 under pressure in presence of $ZnCl_2$ (Vignon).

Basic colouring-matters which owe their basicity to the chromophore and more especially to the auxochrome NH_2, form salts with acids and are used in practice in the form of hydrochlorides, sulphates, etc., from hot acidified aqueous solutions of which wool and silk fix the coloured base. These basic dyes also form insoluble salts with tannin, etc., so that they are capable of dyeing cotton —which has no affinity for basic dyes—if this is previously mordanted by prolonged immersion in cold solutions of tannin extracts (sumac, etc.), followed by fixation of the tannin in another bath containing an antimony, aluminium, or iron salt, or gelatine. In the subsequent dyeing-bath, the dye is fixed rapidly, even in the cold (the fixation is more regular, *i.e.*, slower, in presence of a little alum). The full (intense), bright colours thus obtained on cotton resist the different reagents well but are destroyed during washing by the rubbing. In 1901 C. Favre suggested the use of resorcinol and formaldehyde as mordants in place of tannin.[3]

[1] In addition to what has been already stated with reference to the application of **lakes**, it may be said that they are derived from acid or basic colouring-matters, coloured pigments, or colouring-matters of the anthraquinone group. The soluble acid colouring-matters are precipitated by salts of calcium, barium, strontium, aluminium (chlorides), magnesium (sulphate, etc. Solutions of basic dyes are precipitated by tannin, Turkey red oil, resin, or, more commonly, sodium phosphate or sodium arsenate. Anthraquinone dyes (alizarin, cœrulein, etc.) form lakes with greater difficulty, and it is necessary to observe rigorously the proper temperature conditions. In preparing lakes, great importance attaches also to the substance on which the precipitated lake is deposited or with which it is mixed (aluminium hydroxide, barytes, zinc or lead white, ferric oxide, fresh aluminium silicate, etc.), and of these, the ones more easily decomposable by dilute acids retain the colour best. Lake-formation is hence not a simple absorption phenomenon but also a chemical phenomenon.

[2] There are certain substances which are fixed on mordants even if they contain no hydroxyl groups, such as 1 : 4 : 5 : 8-tetra-alphylaminoanthraquinones (R = an aliphatic group),



. The corresponding tetrahydroxyanthraquinones show affinity only for beryllium mordants, with which they give a deep blue lake, whereas 1 : 4-dihydroxyanthraquinone dyes well with various mordants. Werner showed that even colourless substances may colour certain mordants; thus, dimethylglyoxime yields a deep blue coloration with nickel mordants owing to the formation of complex metallic salts (*see* Vol. I., p. 848).

[3] **Behaviour of Colouring-Matters towards different Fibres and Mordants according**

PHYSIOLOGICAL ACTION OF DYESTUFFS. Certain dyestuffs, even in dilute solution, are very readily fixed by cellular protoplasm and may cause death; thus methylene blue is used for staining bacteria and other microscopic

to Noelting. If a skein of wool, silk, or cotton is immersed for some hours in a solution of a basic ferric salt, the fibres assume a brown colour, having fixed a certain amount of ferric oxide or basic salt. The same holds generally for all salts of oxides corresponding with the formula R_2O_3. The salts of protoxides (RO), *e.g.*, those of copper, iron, manganese, nickel, cobalt, etc., especially the tartrates or in presence of tartar, are fixed by wool or silk, but not at all or but slightly by vegetable fibres.

Not only metallic salts, but also certain organic substances (tannin materials and salts of hydroxyoleic and hydroxystearic (sulpho oleates) acids, can be fixed by fibre.

A large number of colouring-matters are fixed directly on animal fibres in a neutral or acid bath, more rarely in an alkaline bath. To this group belong the nitro derivatives of the phenols and amines: the azo, basic, and acid dyes; basic, acid, or sulphonated derivatives of triphenyl methane; certain phthaleins (fluorescein and eosin); the aminophenazines, safranines, thioindamines, phenoxazine derivatives (gallocyanine and Meldola's blue), phenylacridine complexes (phosphine), quinoline complexes (cyanine, quinoline red, quinophthalones), hydrazides, osazones (tartrazine), ketonimides (auramine) and, among the natural colours, indigo carmine, berberine, safflower, saffron, archil, and catechu. Almost all of these dyes are fixed in minimal quantity or not at all on vegetable fibres. Those which are fixed by the latter are less numerous and include: a first group of substances which are fixed only with difficulty (better with tannin), *e.g.*, certain aminoazo-compounds, phenylene brown, chrysoidine, methylene blue, Victoria blue, safranine; a second group fixed stably and directly and consisting of numerous azo derivatives of benzidine, tolidine, diaminostilbene, *p*-phenylenediamine, naphthylenediamine, diamino azobenzene, diaminoazoxybenzene and its homologues, diaminodiphenylamine, canarine (oxidation product of thiocyanates), and the sulphur dyes of Croissant and Bretonnière; a third group which do not dye wool, cotton, or silk directly but give bright fast colours if these fibres (especially with wool) are previously mordanted with salts of iron, aluminium, or chromium; such are certain phthaleins (gallein), derivatives of anthraquinone (alizarin, purpurin, alizarin orange, anthragallol), anthraquinoline (alizarin blue), phenoxyanthranol (cœrulein), and almost all the *natural colouring-matters* (logwood, cochineal, quercitron, cudbear, sandalwood, etc.). Noelting gave the name *substantive dyes* to those which dye animal and vegetable fibres directly and that of *adjective dyes* to those which dye the fibres only after mordanting.

Certain dyestuffs are fixed directly by wool and silk and only indirectly by cotton, *i.e.*, when the latter has been mordanted. Such are gallocyanine and various carboxylic acids of azo compounds. In dyeing with *aniline black*, the fibre fixes both the aniline salt and also the oxidising agent, the latter oxidising the aniline on the fibre with formation of an insoluble aniline black. Dyes which are not fixed directly by cotton, dye it only after mordanting with tannin or sulpholeic acids if they are basic in character, or after mordanting with metallic oxides, with or without sulpholeates, if they are acid.

Further, various substantive colouring-matters have the property of fixing others on them; for instance, chrysamine and canarine, which are yellow, fix basic colouring-matters, such as magenta forming an orange, malachite green forming a yellowish green, and methylene blue forming a blue colour. All the benzidine colours have the same property, to which Noelting gives the name *secondary dyeing*, a term applicable also to all dyeing with mordants. Direct dyeing would then be *primary dyeing*.

In some cases a third colouring-matter can be superposed; for instance, the violet lake of alizarin and iron combines with methyl violet giving a brilliant triple lake. The red lake of alizarin, alumina, and lime, which is not very bright and rather opaque, is rendered brilliant and more fast by the fixation of a sulpholeate, which forms a quadruple lake; finally, this can still fix tin from a soapy solution of tin salt, a new lake with five components being formed.

If a fabric removed from a solution of a basic iron salt, instead of being washed immediately (in which case it becomes yellowish), is treated directly with alkali or soap (or with a solution of a salt the acid residue of which forms an insoluble compound with oxide of iron), it becomes much more intensely coloured and the quantity of iron fixed by the fibre is considerably increased. Oxide of iron can be accumulated on the fibre, not only, as just mentioned, from an alkaline bath, but also by impregnating the fibre itself with ferrous salts of volatile acids, *e.g.*, the acetate, and then exposing it in the moist state to the air. The ferrous salt is thus converted into basic ferric salt, this in warm, moist air losing part of its acid and undergoing change into an insoluble, highly basic salt, which is not removed from the fibre even by repeated washing.

In order to help the action of the air and render a larger quantity of basic salt insoluble, the fibre may be passed into a bath of cow-dung or lime and potassium silicate, phosphate, or arsenate. Aluminium salts are similarly rendered insoluble by formation of a basic salt. The basic chromium salt is fixed by a subsequent bath of sodium carbonate or, better still, by impregnating the tissue with a solution of chromium sesquioxide in caustic soda and exposing it to the air, the caustic alkali being thus converted into carbonate, which precipitates the sesquioxide of chromium; instead of exposure to the air, the action of steam may be employed. Chromous oxide is precipitated by simple washing of the impregnated tissue with a tin salt. Sulphoricinate is fixed by solutions of aluminium salts, and tannin by solutions of tartar emetic or ferric or aluminium salts.

The action of a chromate bath on catechu is twofold: first, the catechu undergoes oxidation with considerable darkening, and then combination takes place between the oxidation product and the chromium sesquioxide resulting from the reduction of the chromate.

preparations. Formerly, when prepared wih arsenious acid, triphenylmethane dyes were poisonous. More or less poisonous are Victoria orange, aurin, metanil yellow, safranine, orange II, fast yellow, Martius yellow, methyl orange, magenta, acridine red. Methyl violet and auramine are used in ophthalmology and surgery as a bactericide, and methylene blue (base) is employed as an internal analgesic in cases of malaria, carcinoma, etc.

The use of the potassium derivative of dinitro-*o*-cresol (antinonnin) has been suggested to combat the growth of fungi in moist situations and on beams. If fluorescein is injected into the living body it turns yellowish-green in a few minutes, whilst if the body is dead, no change occurs. The use of zinc, copper, barium, etc., salts for salt-formation gives poisonous dyestuffs.

OSTWALD'S NEW THEORY OF COLOURS AND THEIR NUMERICAL DEFINITION (1916–1920). The perception of colour is a psychic phenomenon. *Absolute colours* are those apparent in a dark field, as in emission spectra (*see* Vol. I., p. 57), that is, pure colours uninfluenced by the white light of the surroundings; the latter darkens the colour, what is observed being the *relative colour* resulting by reflections from the luminous surfaces present in relation to their intensity and extent. Thus, if a bright orange-yellow disc is projected on to a dark screen the colour appears in all its purity and brightness, but if white light is projected all round the disc, the latter appears chestnut-colour, that is, is darkened. In practice these *relative colours* are the more important.

Distinction must also be drawn between *non-chromatic colours*, *i.e.*, *greys* comprised between white and black, and *chromatic colours*, comprising the rest (reds, blues, yellows, etc.). *White* is the colour which gives a complete diffusion of the incident light (typical is precipitated barium sulphate). The *ideal black* is that observed on looking into the orifice of a dark wooden box, lined with black silk velvet, but the most intense black practically obtainable in painting still reflects 2 per cent. of the light.[1] A *grey* formed of 51 per cent. of ideal white and 49 per cent. of ideal black appears very light, whilst that appearing to the eye to be the true mean between black and white reflects only 14 per cent. of the light; this is explained by *Fechner's law*, according to which the *excitation* on the organ of sight should increase in arithmetic ratio, because the *sensation* increases in this way. The fact that the *practical mean* grey is formed of 14 parts of white and 86 of black being established, it is possible to make up the whole scale of greys by fixing types judged by the eye.

Similarly, with the chromatic colours, we can form a graduated colour scale by arranging the fundamental colours (yellow, red, blue) at equal distances on the circumference of a circle and interpolating intermediate colours between these. In this way is obtained a *chromatic circle*, in which the differences are greatest for two colours diametrically opposite, these being known as *complementary colours*, since an optical mixture of them yields a neutral grey.

If two moderately near colours a and b on the chromatic circle are chosen, it is always possible to find experimentally a colour c which, when mixed in an equal amount of a, gives b; the distance on the circle between c and b equals that between b and a. Hence any colour can be analysed or defined by this system, but to make such mixtures it is necessary to be able to determine and define the *pure colour* which lends itself to such mixture. To this end Ostwald supposes that every practical chromatic tint is composed of a mixture of white (w), black (b), and pure colour (p), so that $w + b + p = 100$. For a pure colour, $w + b = o$, whilst for a grey, p is zero or $w + b = 100$.

In practice no pure colour, giving a single coloured line in the spectrum, exists, the range of wave-lengths being moderately wide, and Ostwald states

[1] To the question, *Is black a colour?* Ostwald replies that in the region of *absolute colours* black does not exist, but in that of *relative colours* black is a colour, since it does not represent total absence of luminous emanation; this emission may be very slight (even only 0·5 per cent.), but is perfectly determinable.

that any pure colour practically consists of waves corresponding with the half of its chromatic circle.

The practical procedure for the qualitative and quantitative definition and analysis of a colour is as follows. A continuous spectrum is projected on to the coloration; the part on which radiations of the same colour impinge should appear white, but actually appears a greyish white which can be analysed by comparing it with the linear scale of greys, corresponding with known percentages of white and black. It can then be affirmed that, in the colour analysed, there is as much black as there is in this grey. The percentage of white in the original coloration is determined by illuminating the latter with that part of the spectrum which corresponds with its complementary colour, this being easy to define as it makes the coloration appear black or, more accurately, very dark grey. The percentage of white in this dark grey and hence the amount in the original colour are then ascertained by comparison with the linear scale of greys. The percentages of black (b) and white (w) being thus determined, that of the pure colour is: $p = 100 - w - b$. For this analysis, the spectrum used may be replaced by a transparent chromatic screen, through which the colour to be analysed is observed.

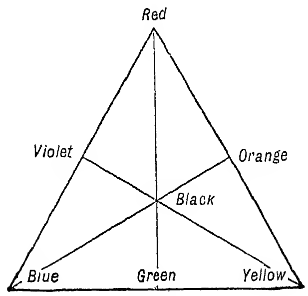


FIG. 469.

Ostwald has collected the principal laws of the new theory in a *colour primer* and has added an atlas of about 3000 colours, so that the analysis of any colour may be made by simple comparison. He has prepared also a *centesimal chromatic circle* containing 100 gently graded colours, any two complementary colours[1] occupying polar positions. The positions of the 100 colours on the circle are indicated by the numbers, 00, 01, 02, to 99. To render the characterisation of any tint more easy, Ostwald has prepared, for each of the 100 colours, an equilateral triangle, the vertices being occupied by pure colour (P), pure white (W) and pure black (B) respectively (*see* Fig. 470). To synthesise any given coloration, that point in one of the triangles is ascertained which agrees exactly with the coloration. The straight line joining this point with the apex p is continued to meet the opposite side, wb, at a point indicating the grey which, together with the pure colour, p, gives the coloration under investigation.

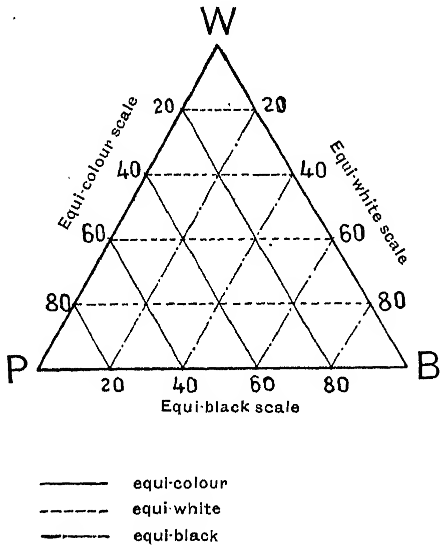


FIG. 470.

Ostwald has attempted to determine

[1] Rosenstiehl's Old Colour System is less perfect, but far simpler, than that of Ostwald. It is based on Young's theory, according to which any coloration is produced in the eye by superposition of three fundamental colour sensations. At the vertices of Maxwell's triangular diagram are placed the three fundamental or primary colours, red, yellow and blue (Fig. 469); colours exactly intermediate to any two of these are the secondary colours (orange, green, violet). Mixture of the colour (material) of any apex with that represented by the mid-point of the opposite side gives black, whilst mixture of the corresponding luminous waves forms white. Rosenstiehl constructed a diagram of 24 colours, representing 12 pairs of complementary colours, the angle between two adjacent colours being 15°.

In 1864 Chevreul prepared a chromatic scale comprising 14,421 colours, and from this Valette and Klinksiec constructed a code of 720 colours.

laws concerning the so-called *harmony of colours*. He points out that every pure colour may vary its tone[1] in three ways; in the intensity or value of the pure colour, thus forming the equi-colour scale; in becoming lighter owing to the presence of more or less white, thus forming the equi-white scale (*Weissgleiche Reihen*); and in becoming darker owing to the presence of more or less black, the equiblack scale (*Schwarzgleiche Reihen*) being formed. For the quantitative definition of the equi-colour scale the chromatic circle may be divided into eight principal zones of colour, starting from yellow (yellow, orange, red, violet, turquoise, sky-blue, green, and yellowish green), and each of these eight zones may be subdivided into three components, the twenty-four components thus obtained being defined quantitatively by the following divisions of the centesimal chromatic circle:

Zone.	Components of each zone.		
	1	2	3
Yellow	00	04	08
Orange	13	17	21
Red	25	29	33
Violet	38	42	46
Turquoise	50	54	58
Sky blue	63	67	71
Green	75	79	83
Yellowish green	88	92	96

In this manner each tint is standardised, and to indicate the white and the black entering into any colour to be synthesised the rules indicated to establish harmony in the non-chromatic colours, *i.e.*, the greys (*see* preceding note), may be followed.

For instance the tint with the *colour index*, 17*l*, *g*, is that occurring in the orange zone in the second component and contains as much white as there is in the grey *l*, and as much black as in the grey *g*. The content in white may range from *c* to *p*, and that in black from *a* to *n*, and as the second letter should always be less than the first, for every tint there are 28 derivatives differing in their contents of white and black. Hence for the 24 fundamental colorations of the preceding table there will be $24 \times 28 = 672$ *chromatic standards*, which are sufficient to satisfy all practical demands.

For each colour there exists an *isochromic triangle*, the chromatic indices for the triangle having the same number whilst the letters exhibit all possible variations. The colours may, however, be disposed so that the letter remains constant whilst the numbers vary, the resulting *equivalent circle* having equal contents of white and black.

The principal *rules of harmony in colours are:* (1) Any colour may be replaced wholly or partially by those of its equi-colour scale, and (2) Any colour may be replaced completely by the colours immediately adjacent to it in the chromatic circle. In general, harmony in colours depends, firstly, on the contents of white and black and, secondly, on the pure colour itself.

During recent years various attempts have been made, without practical success, to utilise the colouring matters produced by certain *chromogenic bacteria*, *e.g.*, *B. prodigiosus*.

[1] More simple are the rules for establishing *harmony in the non-chromatic colours* (white, grey, black). If the linear scale of the greys (*see above*) is divided into, say, 20 equal parts distinguished by the letters *a*, *b*, *c*, etc., *a* will represent white and *b* a very light grey, while beyond *l* the grey becomes almost black and *t* represents the most intense black realisable in painting. For practical purposes these gradations are too close, and the alternate ones, *a*, *c*, *e*, etc., suffice. Such gradations, still equidistant, dominate the whole region of the greys. Arbitrary superposition of three different greys may produce an effect of incoherence or discord, but harmony is obtained if three equidistant gradations, such as *c*, *e*, *g* or *a*, *g*, *n*, are chosen.

MANUFACTURE OF COLOURING-MATTERS

Since 1856–1860, when Perkin in England made mauveine and Renard and Frank in France made fuchsine (magenta) on an industrial scale, scientific progress in colouring-matters has advanced *pari passu* with the industrial development.

In the history of the artificial colouring-matters, side by side with the names of the scientific men, such as Perkin, Williams, A. W. Hofmann, Graebe, Liebermann, Baeyer, Witt, Nietzki, Noelting, Caro, etc., who laid the first stones in this marvellous chemical edifice, are those, not less worthy, of the brilliant and daring industrial workers who, by uninterrupted energy and the application of ingenious processes, carried these theoretical discoveries into the larger field of industry and commerce.

The dye industry, although not born on German soil, has there reached its greatest development and borne its richest fruit, far in excess of the dreams of its founders. This result has been reached in Germany as a result of various fortunate circumstances.[1]

[1] At first France was at the head of the aniline dye industry, with numerous pioneers, such as Verguin, Renard Brothers, Frank, Poirrier, Guinon Marnas and Bonnet, Coupier, Girard and de Laire, Baubigny, Persoz, Bardy, Lauth, Kopp, Rosenstiel, Roussin, etc., but of all these very few have been able to withstand the wonderful organisation of the large German manufacturers. Even England, the cradle of the industry, is now in a position greatly inferior to that of Germany. The six English factories working in 1913 employed altogether 35 chemists, whilst the six largest German firms employ 600, besides 350 engineers and technical directors. From 1886 to 1900, the English firms took out 86 patents, while the six more important German ones took out 948.

The principal English firms producing dyes were: Brooke, Simpson, and Spiller, London; The Clayton Aniline Company, Manchester; Read, Holliday, and Sons, Limited, Huddersfield; and I. Levinstein and Company, Limited, Manchester.

The German firms which enjoyed almost a monopoly of the world's trade in aniline colours were: (1) Badische Anilin- und Soda-Fabrik, Ludwigshafen; (2) Farbenfabriken vormals Fr. Bayer und Co., Elberfeld; (3) Farbwerke vormals Meister, Lucius und Brüning, Höchst; (4) Leopold Casella and Co., Frankfort; (5) Actien-Gesellschaft für Anilin-Fabrikation, Berlin; (6) Kalle and Co., Biebrich; of less importance are the firms of Oehler in Offenbach, Leonhardt of Mulheim, etc. Firms (1), (2), and (5) work together to regulate the output and trade, and the same is the case with (3), (4), and (6). In 1916 these two federations, together with other companies, united to form a syndicate, termed the Interessengemeinschaft, with a capital of 1,000,000,000 marks. In connection with this syndicate another company was formed, with a capital of 500,000,000 marks, for the manufacture of synthetic ammonia. The dividend paid by this vast organisation was 12 per cent. in 1918, 18 per cent. in 1919 and 20 per cent. in 1920.

Of the German factories, the Badische Anilin- und Soda-Fabrik alone, with a capital of over £1,400,000, employed in 1908 about 8000 workmen (in 1896 less than 5000 and in 1865, the first year of working, 30), and more than 160 chemists and 75 engineers; for more than 20 years before the war the dividends paid by this company had been about 25 per cent.

The Bayer Company of Elberfeld employed, in its various works, 170 chemists, 35 engineers, and about 6000 workmen. Its principal works were originally at Elberfeld, but the most important of their manufactures—colouring-matters, pharmaceutical and photographic materials were transferred several years ago to a new factory at Leverkusen, near Cologne, which occupies an area of 529 hectares and in 1912 found employment for 4000 workpeople. The company, starting from the idea that the *employer owes to the employee more than his wages*, has created a number of institutions which in 1912 represented a total capital of £600,000. Among these was a library of 12,000 volumes used by 44 per cent. of the workpeople, the books demanded in 1907 consisting of popular works on scientific subjects to the extent of 52 per cent. and of miscellaneous literature to the extent of 48 per cent.; the library committee consists of chemists, engineers, and workmen. Five hundred baths were built, 150,000 baths being taken annually. There were dormitories with beds at 2½*d.* per night, refectories which supply the three meals of the day to men for a shilling and to boys and girls for 9*d.* There were also free technical schools and schools of art and music. A lying-in hospital (also for wives of workmen not employed in the factory) cost £7200, the annual expenses being £1600. A hall for theatrical performances and conferences, another for lectures, concerts, etc., and a third for conferences of workmen, cost £18,000. There were sickness funds, savings banks, and a life insurance scheme, supported to the extent of two-thirds by the funds of the company; also old-age pensions, and accident funds in addition to the State fund, the company paying for the first three days after the accident (not paid by the insurance companies) and supplementing the legal payment by 50 per cent. The sale of alcoholic drinks—beer included—is forbidden in the refectories, but coffee, tea, milk, etc., are obtainable at very low prices. On all these institutions the Bayer Company spent more than £80,000 annually and was yet able to pay its shareholders a dividend of 25 to 30 per cent. on a capital of £1,200,000.

The scientific and technical work of the company is indicated in the 4000 patents filed up to the year 1907.

To the *world's output* of dyestuffs Germany contributed in 1913, 75 per cent.; Switzerland, 7·5 per cent.; Great Britain, 6 per cent.; France, 5 per cent.; United States, 3·5 per cent.; Austria, 1·6 per cent.; Russia, 1·1 per cent.; and Belgium, 0·6 per cent.

In 1912 the total amounts of the principal dyestuffs made were:

	tons	
Indigo (100 per cent.)	8000 at £400 per ton	£3,200,000
Sulphur, black	15,000 at £80 ,,	£1,200,000
Various sulphur dyes	5000 at £80 ,,	£400,000
Azo dyes	60,000 at £80 ,,	£4,800,000
Triphenylmethane dyes, etc.	10,000 at £240 ,,	£2,400,000
Anthracene dyes, etc.	6,000 at £240 ,,	£1,440,000
Various dyes	6,000 at £120 ,,	£720,000
Total	110,000 Total	£14,160,000

Of these, the United States consumed 26,000 tons; Great Britain, 19,000; Germany, 15,000; France, 9500; Russia, 10,000; Italy, 8000; other countries, 22,500.

The prime materials for dyes—besides sulphuric, nitric and hydrochloric acids, sodium carbonate and hydroxide, ammonia, lime, etc.—are the various aromatic hydrocarbons obtained from tar, which may, however, be first transformed into substances more active chemically (phenols, amines, etc.), *i.e.*, the so-called *intermediates*.

The fundamental reactions to which the distillation products (benzenes, phenols, naphthalene, pyridine, etc.) of tar are subjected consist, in general, of *nitration*, *reduction*, *diazotisation*, *sulphonation*, *fusion* with caustic soda, *chlorination*, and *oxidation*.

These reactions lead to intermediate products very near to the true colouring-matters. Thus, nitrobenzene and its homologues yield aniline, toluidine, etc., by simple reduction with iron turnings and hydrochloric acid, and aniline then gives diphenylamine, dimethylaniline, sulphanilic acid, etc.

Oxidation of aniline, toluidine, etc., gives fuchsine (magenta), safranine, methyl violet, etc. The nitroanilines serve for the preparation of azo-dyes, while the action of sulphur on amines leads to primuline and the new class of sulphur-dyestuffs.

With another reducing agent ($Zn + KOH$), nitrobenzene gives other products (hydrazobenzenes, etc.), from which other classes of colouring-matters originate.

A further important reaction consists in the introduction of sulphuric acid residues (**sulphonic group**, SO_3H) into benzene (or naphthalene) nuclei in place of hydrogen or other groups by treatment of benzene derivatives with concentrated sulphuric acid. The resulting sulphonic acids are of great importance and often decide whether a dyestuff is *acid* in character and hence able to dye wool and silk directly in an acid bath, or *neutral* (or almost so) and capable of colouring cotton directly, or still *basic* and able to dye cotton mordanted with tannin or wool and silk directly in a neutral or faintly alkaline bath.

Many of the Russian and French factories were branches of German ones.

In point of magnitude, the German firms are immediately followed by those of German Switzerland (Basle): Gesellschaft für chemische Industrie; Durand, Huguenin & Co.; Geigy; Kern and Sandoz, etc.

During the European War, when Germany was isolated, attempts were made in France, Great Britain, America and Italy to develop the manufacture of dyestuffs, assistance being accorded by the respective States. In the United States such attempts met with considerable, if not complete, success. In Great Britain various projects were supported to the extent of some millions of pounds sterling without, however, achieving all the results desired, and this country is far from being emancipated from German importations.

The sulphonic group, in its turn, may be replaced by hydroxyl by fusion of the sulphonic acid with caustic soda, this being a very important reaction, as it allows of the ready preparation of resorcinol and of **alizarin**. The OH group may also be introduced into the molecule directly by means of the Bohn-Schmidt reaction, which consists in treating various substances in the hot with sulphur trioxide dissolved in concentrated sulphuric acid.

Oxidation is likewise of great value and was first used for preparing magenta, safranine, etc. It has been found that naphthalene can be oxidised with sulphuric acid in presence of mercury, giving phthalic and anthranilic acids at a cost so low as to admit of the competition of artificial **Indigo** with the natural product (*see* p. 760).

The methods of dyeing textile fibres are becoming continually more simple and more certain and capable of giving the most varied colours. Nowadays stable dyes can be produced directly on the cotton fibre in a single operation, starting with simple chemical reagents.

CLASSIFICATION OF COLOURING-MATTERS

Nietzki divides the artificial organic colouring-matters into the following general groups, with reference especially to their chemical composition:

I. Nitro- colouring matters. II. Azo- colouring-matters. III. Derivatives of hydrazones and pyrazolones. IV. Hydroxyquinones and quinoneoximes. V. Diphenyl- and triphenyl-methane colouring-matters. VI. Derivatives of quinonimide. VII. Aniline black. VIII. Quinoline and acridine derivatives. IX. Thiazole colouring-matters. X. Oxyketones, xanthones, flavones, and coumarins. XI. Indigo and similar and other natural colouring-matters. XII. Sulphur colouring-matters.

For practical dyeing, however, more importance is attached to the division into the following five groups on the basis of the behaviour of the colouring-matters towards different textile fibres, since in practice it is more important to know if a colouring-matter is basic or acid, or if it dyes with or without mordant, than to know if it is a nitro-compound, quinone, hydrazone, etc.:

1. *Basic colouring-matters*, which in a neutral bath dye animal and vegetable fibres; the latter should, however, be previously mordanted with tannin.
2. *Acid colouring-matters*, which dye animal fibres in an acid bath.
3. *Adjective or mordant colouring-matters*, which dye fibres mordanted with metallic oxides (of iron, chromium, aluminium, etc.).
4. *Almost neutral or substantive colouring-matters*, which, as alkali salts, dye vegetable textile fibres directly, without mordanting.
5. *Insoluble colouring-matters or pigments* are formed directly on the fibre, *i.e.*, are used for vat-dyeing or are developed on the fibre.

I. **NITRO-COLOURING-MATTERS.** All the nitro-derivatives of the amines and phenols are energetic dyestuffs, those of the phenols especially being markedly acid colouring-matters, since the *chromophore* NO_2 reinforces the acid character of the OH group. Even the basic substances may become acid if many NO_2 groups are present. It is particularly the salts of these compounds which are coloured; *p*-nitrophenol, for example, is colourless whilst its salts are yellow.

The coloration of the nitrophenols disappears if the phenolic groups are etherified by alkyl groups.

Of the nitrophenols the ortho-products ($OH : NO_2 = 1 : 2$) are the more important and the more highly coloured. Examples are: **Picric acid** (*trinitrophenol*), $C_6H_2(NO_2)_3 \cdot OH$; **Naphthol yellow S** = sodium salt of *dinitronaphtholsulphonic acid*, $C_{10}H_4(NO_2)(NO_2)(OH)(SO_3H)$ (2 : 4 : 1 : 7); **Victoria yellow** (or Victoria orange) = *dinitrocresol*, $C_6H_2(OH)(CH_3)(NO_2)_2$.

II. **AZO-COLOURING-MATTERS.** The azo-colouring-matters, unlike other groups, have retained their original importance, not only owing to the number that can be produced, but especially because the gradations of colour and the stability can be modified

at will. Thus, the azo-group includes *substantive dyestuffs,* which dye cotton without a mordant, wool colouring-matters fast to milling and to sulphuring, and stable adjective dyes such as alizarin.

Their basic chromophore is $—N = N—$ and the chromogen, $R—N = N—R'$, R and R′ being aromatic radicals.

These compounds form the largest and perhaps the most important group of artificial colouring-matters. They are not of themselves (especially in the case of the more simple ones, such as azobenzene) intense dyestuffs, but they become such on the introduction into the benzene nuclei of acid (OH) or basic (NH_2) auxochromes, and with increase of the number of these the intensity increases, passing from yellow to red, to blue or to brown. Blues are obtained with several chromophores $—N = N—$ (di- and tetra-azo-compounds), while naphthalene groups give reds. The higher the molecular weight the more intense becomes the colour.

In certain cases it must be assumed that these auxochromes are united in some way with the chromophore, and, since β-naphthazobenzene no longer exhibits phenolic character, Liebermann attributed to it the structure $C_6H_5—NH—\underset{\diagdown\;\diagup\atop O}{N—C_{10}H_6}$, instead of the ordinary constitutional formula $C_6H_5 \cdot N : N \cdot C_{10}H_6 \cdot OH$.

Certain azo-compounds show behaviour recalling that of quinones and ketones, *e.g.*, they combine with sodium bisulphite. In such case, the formula is represented thus: $C_6H_5 \cdot NH \cdot N : C_6H_{10}O$.

Almost all azo-compounds dissolve in concentrated sulphuric acid, giving a characteristic coloration, which, in general, serves for their recognition and distinction from other colouring-matters (*see* Table *given later*).

Substituted azo-compounds are always obtained by coupling a diazo-compound with a phenol or with an amine, and, in the latter case, diazoamino-compounds are formed as intermediate products.

The first azo-dyestuff of industrial importance (triaminoazobenzene) was prepared in 1867 by Caro and Griess, and it was only with the dyes discovered by Witt and Roussin subsequently to 1876 that this group assumed a position of practical importance.

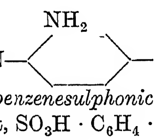
After 1880 azo-colouring-matters again came to the front owing to the preparation of direct dyes for cotton, and later these dyes were produced directly on the cotton fibre, new dyeing methods being thus created.

They are prepared industrially by first diazotising the amine, or its sulphonic acid diluted with water, by means of hydrochloric acid and sodium nitrite, the mass being cooled with ice and tested with starch-potassium iodide paper so as to avoid any large excess of nitrite. After diazotisation, the *coupling* is carried out by pouring the whole slowly into an alkaline solution of the phenol, the mass being kept alkaline. The colouring-matter thus formed is separated in an insoluble state on addition of salt and is then filter-pressed. The reaction between the amines and the diazo-compounds is more complex: $R \cdot NH_2,HCl(+ \frac{1}{2}N_2O_3) \longrightarrow R \cdot NCl \vdots N(+ R' \cdot OH, \text{phenol}) \longrightarrow HCl + R \cdot N : N \cdot R' \cdot OH$. The diazo-group enters in the para-position to H, OH, or NH_2, or if this is occupied, in the ortho-position.

Azo-colouring-matters are so numerous and so varied in constitution and behaviour that they may be divided into several sub-groups.

The **MONOAZO-COMPOUNDS** may be sulphonated (aminoazo-derivatives give basic colouring-matters and the hydroxyazo-derivatives without carboxyl, acid colouring-matters) or not sulphonated (the aminoazo-compounds give basic and acid colouring-matters and the hydroxyazo-compounds basic and adjective colouring-matters). **POLY-AZO-COMPOUNDS** yield substantive and adjective dyestuffs (*i.e.*, without benzidine nuclei, and then form acid, basic, and mordant colouring-matters). Finally there is the sub-group, the members of which are generated directly on the cotton fibre.

(*a*) **Aminoazo-derivatives.** These are obtained in the usual way, in the cold and in alkaline solution, from diazo-compounds (amino- or not) and amines.

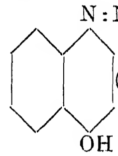
Among these are *fast yellow, acid yellow, tropæolin, chrysoidin* [$C_6H_5 \cdot N : N—$  —NH_2,HCl], the *oranges, Indian yellow* (*nitro-derivative* of *phenylaminoazobenzenesulphonic acid*), *orange IV* or *tropæolin OO* (sodium salt of the non-nitrated product, $SO_3H \cdot C_6H_4 \cdot$

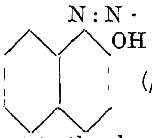
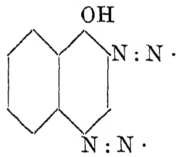
$N:N \cdot C_6H_4 \cdot NH \cdot C_6H_5$) and *vesuvine* or *Bismarck brown*, which is the hydrochloride of *triaminoazobenzene*, $NH_2 \cdot C_6H_4 \cdot N:N \cdot C_6H_3(NH_2)_2$, mixed with $C_6H_4[\cdot N:N \cdot C_6H_3(NH_2)_2]_2$.

Indoin is a basic blue obtained by coupling diazotised safranine with β-naphthol.

On textiles they are not very fast to light, the less fast being those which do not contain the sulphonic group. In printing textiles these colours are corroded by the stannous chloride.

(*b*) **Hydroxyazo-derivatives** (or *azoxy-compounds*), *e.g.*, hydroxyazobenzene, $C_6H_5 \cdot N:N \cdot C_6H_4 \cdot OH$. *Tropæolin O* is a dihydroxyazobenzenesulphonic acid.

Of greatest importance are the derivatives of α- and β-naphthols,  (α)

and  (β), the compounds with the auxochrome in the *ortho* : β-position with respect to the chromophore (· N : N ·) being colouring-matters of greater fastness to acid and alkali than the *ortho* : α-compounds. If, however, another azo group be introduced into the latter, it will occupy the β-ortho-position, , the fast brown dyestuffs being obtained.

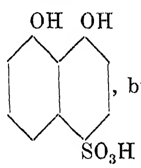
Those most used are the sulphonic derivatives, obtained from various *naphtholsulphonic acids.*

Of the numerous colouring-matters of this group, the most important are: *orange II* [1], *tropæolin OOO N. II* or *N. I*, *croceine orange*, *orange G*, etc., *Ponceau* (various), *Bordeaux S amaranth*, *rocelline*, *croceine*, *azorubin S* $\left(\begin{array}{l} N{-}C_{10}H_6 \cdot SO_3H \ (4) \\ \| \qquad\qquad\quad OH \quad (1) \\ N{-}C_{10}H_5 \langle \ SO_3H \ (4) \end{array}\right)$, etc.

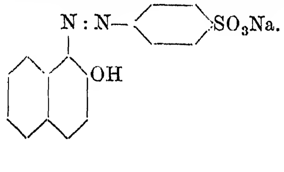
(*c*) **Azo-Colouring-Matters derived from Carboxylic acids** are obtained from carboxylic diazo-compounds and phenols or amines.

These compounds (especially the *o*-hydroxycarboxylic acids, such as salicylic acid) have an affinity for metallic mordants, particularly for chromium oxide. The hydroxyl and carboxyl groups are in the ortho-positions.

Among the nitrobenzeneazosulphonic acids are *alizarin yellow*, the *diamond yellows*, etc., which, on cotton and wool, give colours very resistant to light and to fulling. The hydroxy-azo-acids include various tropæolins (V, R, O, OOO, etc.), *chrysoin*, *cochineal scarlet*, *ponceau*, *palatine scarlet*, etc.

(*d*) **Azo-Colouring-Matters derived from Dihydroxynaphthalenes.** Several of these compounds are fixed by mordants when they have two hydroxyl groups in the ortho (1 : 2) or peri (1 : 8) position, as in anthraquinone (*see* Alizarin) and , but these com-

[1] *Orange II*, prepared from diazotised sulphanilic acid and β-naphthol, has the constitution:

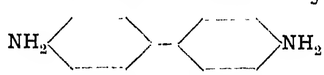


pounds are used practically, not on mordants, but for the dyeing of wool, as they give very regular results (such are the *azofuchsines*), while the peridihydroxynaphthalenes are used on mordants and form the so-called *chromotrope* colouring-matters, which dye unmordanted wool in an acid bath, giving a fine red turned violet by addition of alumina mordants or blue-black with chrome mordants.

POLYAZO-COLOURING-MATTERS (di- and tetra-azo) contain the chromophore $\cdot N:N\cdot$ several times and vary according as the chromophores are in the same benzene nucleus or in different nuclei and as the auxochromes are or are not in the same nuclei as the chromophores.

Here are found benzidine derivatives in which the two chromophores are in two different nuclei, joined by a single linking.

Among the sulphonic derivatives are, for example, *Biebrich scarlet*, and the croccines, while among the polyazo-compounds are also *naphthol black*, *naphthylamine black D diamond black* (which is obtained from aminosalicylic acid and is fixed by mordants), etc.

BENZIDINE,  (*see* p. 718), when treated with nitrous acid, gives a tetrazo-derivative which yields yellow, red, blue, or violet colours on combination with amines or phenols. With naphthionic acid, tetrazodiphenyl gives *Congo red*, which was the first substantive dyestuff obtained and was patented by C. Böttiger in 1882:

$$\begin{array}{l} C_6H_4 \cdot N:N \cdot C_{10}H_5 < \begin{array}{l} SO_3H\ (\alpha) \\ NH_2\ \ (\alpha) \end{array} \\ | \\ C_6H_4 \cdot N:N \cdot C_{10}H_5 < \begin{array}{l} SO_3H\ (\alpha) \\ NH_2\ \ (\alpha) \end{array} \end{array} ;$$

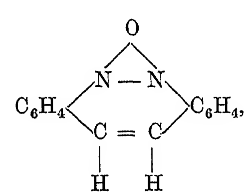
the free sulphonic acid is blue while the salts are red and are fixed *directly on cotton*, but have the disadvantage of becoming blue or black in contact with even weak acids.

The Benzopurpurines (*see* p. 719) are obtained in a similar manner.

These benzidine derivatives cease to form substantive colouring-matters if the meta-positions (with respect to the NH_2) are occupied.

Substantive or direct colours, when fixed on cotton, function as weak mordants for basic dyestuffs.

The different firms making colouring-matters place on the market a large number of substantive dyes under various names. For instance, Messrs. Cassella have a long and important series of *diamine colours* (diamine yellow, green, red, black, blue, etc.), while Meister, Lucius und Brüning call their substantive colouring-matters *dianil colours*. The Bayer Company have the most numerous and important series of substantive dyes, which they term *benzidine* or *benzo dyestuffs* (*e.g.*, benzo azurines, benzo browns, benzo reds, etc.). The Actien-Gesellschaft für Anilin-Fabrikation, Berlin, call these dyes Columbia, Zambesi, etc.

The Derivatives (*e.g.*, *sulphonic*) of azoxystilbene, , have the *special property* of dyeing cotton directly in an *acid bath*.

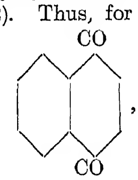
The firm of Meister, Lucius und Brüning, in 1896, placed on the market a class of strongly basic colouring-matters (*Janos dyes*), which colour cotton directly—without previous mordanting—in an *acid bath* and also dye with the same colour the wool and cotton of a mixed fabric when the latter is boiled in a bath acidified with sulphuric acid. These dyes change their tint temporarily if brought into contact with hot objects (hot iron).

Of very great importance is the group of azo-dyes produced directly on the fibre by processes of diazotisation and combination, these bearing the name of Ingrain Colours.

Cotton fabrics or yarns are impregnated in the cold with a base (aniline, *p*-nitraniline, aminoazobenzene, benzidine, safranine, etc.), or they may be first dyed with one of the substantive tetrazo-dyes containing free auxochrome amino-groups (*e.g.*, diamine black, primuline yellow, benzo brown, blue, or black, etc.). They are then transferred for 15 minutes to a wooden vessel containing a cold *diazotising* solution, this consisting, per 100

kilos of cotton, of 2000 litres of water, 2 to 4 kilos of sodium nitrite, and 6 to 10 kilos of hydrochloric acid at 20° Bé.; this diazotisation is carried out in dimly lighted rooms, since sunlight readily decomposes the diazo-compounds formed. After removal from this bath, the cotton is allowed to drain for a short time and is then placed in a *developing bath* (*coupling bath*) containing 2000 litres of water, 0·5 kilo of sodium carbonate and 0·5 to 1 kilo of β-naphthol previously dissolved in 415 to 430 grms. of caustic soda solution at 40° Bé. The cotton is manipulated rapidly and in a few minutes intense development of the colour takes place. When substantive dyestuffs are thus further diazotised on the fibre, they exhibit increased fastness to scouring, and this is still more the case if the fabric is subsequently treated with a bath of potassium or sodium bichromate at 90° to 95° for 20 minutes; a final copper sulphate bath at 50° for 25 minutes gives greater fastness to light, but both copper and chromium compounds diminish the brightness of the colour to some extent, and on this account the firm of Geigy suggests the use of a final bath of formalin. Instead of β-naphthol, α-naphthol, resorcinol, phenylenediamine, *benzonitrole* (diazotised p-nitraniline), etc., may be used.[1] By this method of diazotising and developing on the fibre the original tint of the basic substance is intensified, certain yellows become orange or scarlet (p-nitraniline gives with β-naphthol a fine scarlet similar to Turkey red, while with α-naphthol it yields a violet-red), certain reds become brown or even blue, the blues become intense blacks, etc. Different developers give different colours or shades.

The coupling of a phenol with a diazo-compound is prevented by the presence of a reducer which destroys the latter; as reducing agent stannous chloride was at one time used, but use is now made of sodium or zinc hydrosulphite, which permits of the printing of textiles in white designs on a coloured ground.

III. HYDRAZONE AND PYRAZOLONE COLOURING-MATTERS. Hydrazones are obtained by the action of phenylhydrazine, $C_6H_5 \cdot NH \cdot NH_2$, on compounds containing ketonic groups (*see* p. 252). Thus, for example, the condensation of phenylhydrazine with α-naphthaquinone, , gives a hydrazone of the constitution $C_6H_5 \cdot NH \cdot N : C_{10}H_6 : O$. The same compound is obtained by the interaction of α-naphthol and diazobenzene, so that its constitution might be that indicated by the equation:

$$C_6H_5 \cdot N_2 \cdot Cl + C_{10}H_7 \cdot OH = HCl + C_6H_5 \cdot N : N \cdot C_{10}H_6 \cdot OH,$$

one hydrogen atom being mobile and oscillating between nitrogen and oxygen. The hydrazones may hence be regarded as azo-compounds and can be prepared from diazo-derivatives and phenols. This is true for aromatic compounds (which can be diazotised), but not for those of the aliphatic series, which are only exceptionally diazotised; in the latter case, the hydrazones must be obtained by means of phenylhydrazine.

The colouring-matters of the hydrazone group have not as yet been practically applied, as they are too weak. It was formerly thought that tartrazine was a hydrazone, but Anschütz showed it to be a pyrazolone. In general the **Tartrazines** are obtained by condensing, in hot acid solution, the aromatic hydrazines (sulphonated) with dihydroxytartaric acid, $CO_2H \cdot C(OH)_2 \cdot C(OH)_2 \cdot CO_2H$, which probably reacts with phenylhydrazine as a true di-ketone, $CO_2H \cdot CO \cdot CO \cdot CO_2H$, giving

$$\begin{array}{l} CO_2H \cdot C : N \cdot NH \cdot C_6H_4 \cdot SO_3H \\ \quad\quad\quad\;\, | \\ CO_2H \cdot C : N \cdot NH \cdot C_6H_4 \cdot SO_3H \end{array};$$

a molecule of water is then lost from a carboxyl- and an imino-group,

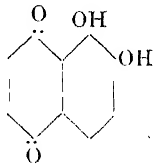
$$N\!\!\begin{array}{l} \diagup N(C_6H_4 \cdot SO_3H) \cdot CO \\ \quad\quad\quad\quad\quad\quad\quad\quad\quad\;\; | \\ \diagdown\!\!-\, C(CO_2H) \text{——} C : N \cdot NH \cdot C_6H_4 \cdot SO_3H. \end{array}$$

The sodium salt is used as a fast yellow for wool, in an acid bath. Some tartrazine nitrates are fixed also by mordants. In an acid bath tartrazine dyes wool a bright and fairly fast yellow.

[1] O. N. Witt (1913) avoids diazotisation on the fibre (with saving in ice) by using p-nitrobenzenediazonium in the form of the crystallised double salt obtained by condensation with sodium naphthalenesulphonate, $NO_2 \cdot C_6H_4N : N \cdot SO_3 \cdot C_{10}H_7 + SO_3Na \cdot C_{10}H_7 + H_2O$. Such salts are non-explosive and highly stable, even at 60° to 70°, and dissolve in water.

IV. COLOURING-MATTERS DERIVED FROM QUINONES AND QUINONOXIMES. All these colouring-matters give very fast tints on fibres mordanted with metallic oxides, with which they form lakes. If the hydroxyl groups present are not in the ortho-position with respect to one another and to the chromophore CO <, the lakes formed have no affinity for the fibres.[1]

The most important colours of this group are formed by int oducing into the chromophores, naphthalene groups; *e.g.*, **Naphthazarin**, which is a *dihydrox naphthaquinone*,



The quinonoximes contain the group : N · OH in place of the ketonic oxygen; they have properties similar to the hydroxyquinones, and here too the affinity for metallic mordants is most marked in the derivatives of the orthoquinones. A few colouring-matters derived from the oxime O==NOH, are known, *e.g.*, *fast green for cotton, naphthol green*, etc.[2]

Among these quinone derivatives are almost all the alizarin (*see* p. 734 and anthracene (*see* p. 731) colouring-matters, purpurin, etc., in all gradations from yellows to reds, blues, blacks, greens, etc.

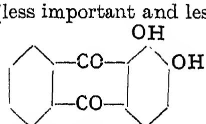
For hundreds of years **alizarin** was the sole epresentative of a group of excellent colours, and was only obtained naturally mixed with purpurin, from which it was separated with difficulty. Nowadays, not only is alizarin prepared artificially, but there are quite fifty other colouring-matters of this group, fast to light and chemical and atmospheric reagents.

While nature yields colours such as madder and indigo in an impure condition (as these are secondary products of vegetable life) and not directly applicable for dyeing, the artificial products are highly pure, much brighter in colour and more easily utilisable as dyes.

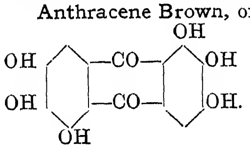
Alizarin and anthracene dyes, which are the prototypes of *mordant colouring-matters*, are used in large quantities for the fast dyeing of wool for clothing and military uniforms. As a rule the wool is mordanted first, by boiling for an hour with an aqueous solution containing 2 to 3 per cent. of potassium dichromate and 1 per cent. of sulphuric acid and amounting to 15 to 20 times the weight of the wool. After mordanting, the wool is rinsed well in water and dyed in a solution of the dyestuff faintly acidified with acetic acid; this bath is heated very gradually to boiling, the latter being maintained for 1 to 2 hours to obtain the maximum intensity and fastness. If fresh addition of the colouring-matter is necessary in order to obtain the desired shade, it is best first to lower the temperature of the bath to 40° to 50° with cold water in order to prevent non-uniformity of tint.

V. DIPHENYL- AND TRIPHENYL-METHANE COLOURING-MATTERS, $CH_2 < {C_6H_5 \atop C_6H_5}$ and $C_6H_5—CH < {C_6H_5 \atop C_6H_5}$. It has been shown on p. 764 that in these colouring-

[1] Mordant colouring-matters are generally obtained with the following groups in the ortho-position: OH and NO (or CO and NOH), 2NOH, 2OH. Also, according to Noelting (1909), in the anthraquinone series intense mordant dyes are obtained also with OH and NH_2 in the ortho-position (less important and less intense are those with OH and NH_2 in the para-position).

[2] Alizarin, , dyes red either cotton mordanted with alumina or wool mordanted with chromium.

Anthracene Brown, or *alizarin brown* or *anthragallol* (tri- to hexa-hydroxy-anthraquinone),



matters the *chromophore* consists of the benzene group with two double linkings in the para-position, R = C=.

The mode of formation and the general properties of diphenyl- and triphenyl-methane derivatives were described on pp. 719, 720.

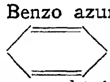
In this group are found **Auramine** (basic)[1] and **Pyronine** (also basic) which dye wool in an acid bath and cotton mordanted with tannin.

The rosaniline group embraces all the basic colouring-matters derived from triphenylmethane, *e.g.*, *malachite green*, *methyl violet*, *formyl violet*, *fuchsine*, etc., while with sulphonic and other groups, acid dyes are obtained, such as *patent blue* (*carmine blue*), *acid fuchsine*, etc.

There are also azo-derivatives of triphenylmethane, such as **Rosamine**, which dyes silk violet-red with a yellow fluorescence, and has the formula:

$$C_6H_5 \cdot C \begin{cases} C_6H_3[N(CH_3)_2] \\ C_6H_3[N(CH_3)_2Cl] \end{cases} O.$$

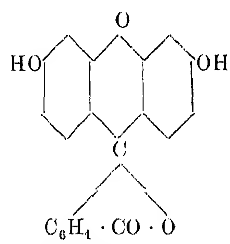
The **Rosolic Acid** group, O == $C < \begin{matrix} C_6H_3(CH_3) \cdot OH \\ C_6H_4 \cdot OH \end{matrix}$, formed by fusion of phenol with oxalic acid in presence of concentrated H_2SO_4, also furnishes numerous colouring matters, *e.g.*, *aurine*, *coralline*, *pittacal*, *chrome violet*.

Benzo azurine is formed from 1 mol. of phenylchloroform with 2 mols. of phenol: O :: $C < \begin{matrix} C_6H_4 \cdot OH \\ C_6H_5 \end{matrix}$; these colouring-matters, which have no practical application, are obtained by the condensation of phenols with phthalic anhydride:

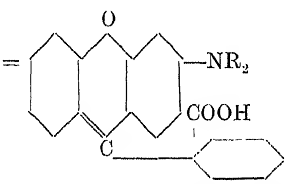
$$C_6H_4 \begin{cases} CO \\ CO \end{cases} O + 2C_6H_5 \cdot OH = H_2O + C_6H_4 \begin{cases} C(C_6H_4 \cdot OH)_2 \\ CO \end{cases} O.$$

Phenolphthalein

Phthaleins (*see* p. 685) with the hydroxyls in the para-positions are of some importance: if resorcinol, $C_6H_4(OH)_2$, is used in place of phenol, **Fluorescein** (the sodium salt of which is uranine) is obtained:

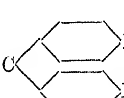


while if dimethylaminophenol is taken instead of resorcinol, or if fluorescein chloride is heated with a secondary amine, NHR_2, fine red colouring-matt: rs, **Rhodamines**, which are basic in character, result:



If previously brominated phthalic anhydride is used, the **Eosins** are obtained:

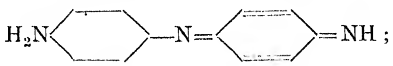
$$\begin{matrix} C_6H_4 \cdot C \begin{cases} C_6HBr_2(ONa) \\ C_6HBr_2(ONa) \end{cases} O; \\ CO - O \end{matrix}$$

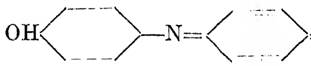
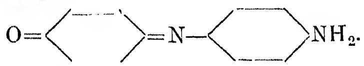
[1] Auramine has the formula H_2 : NCl : C$N(CH_3)_2$, $N(CH_3)_2$.

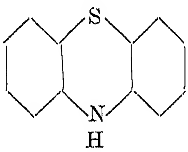
these give beautiful fluorescent red colours on silk but are not very fast to light (*see* p. 685).

VI. **COLOURING-MATTERS OF THE QUINONIMIDE GROUP.** To this belong the derivatives of indophenol and indamine.

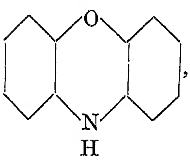
Of the hypothetical quinonimides,  and  various derivatives and condensation products are known, *e.g.*, **Indamine**,



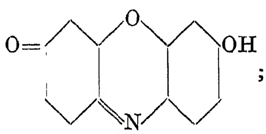
Indophenol,  

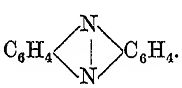
The **Thiazones**, *e.g.*, *thiodiphenylamine*,  with indamines form **Thiazimes** (*e.g.*, *Lauth's violet* or *thionine, methylene blue*,[1] *methylene green*, etc., which are basic dyes).

The **Oxamines** and **Osazones** have an oxygen atom in place of the sulphur of thiazones,

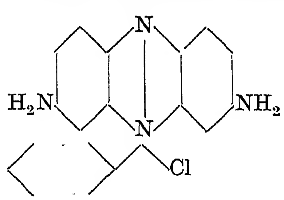


, and undergo various condensations: *Capri blue, naphthol blue, Nile blue*, etc., which are also basic.

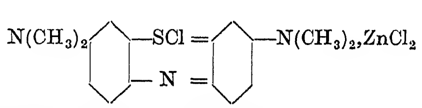
The **Cyanamines** are related to Nile blue; **Resorufin** is an osazone, namely, hydroxy-diphenosazone,  ; **Gallocyanine**, $C_{15}H_{12}O_5N_2$, is obtained by heating nitrosodimethylaniline with gallic acid in alcoholic solution. They dye chrome-mordanted wool a very fast violet, and are used in printing linen, which is treated with sodium bisulphite and chromium acetate and subsequently steamed.

The **Azines** were formerly called **Safranines**; the simplest type is **Phenazine**,  The *eurodines* are used for dyeing cotton mordanted with tannin.

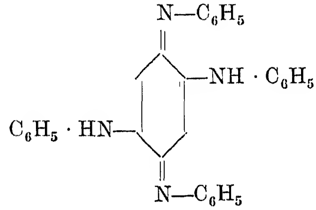
The **Safranines** contain four nitrogen atoms and three aromatic nuclei:

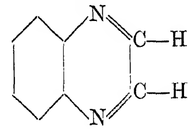


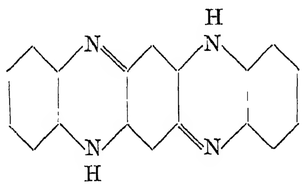
and are strongly basic and give red colours on cotton mordanted with tannin.

[1] Methylene blue,  , is a basic dye which colours cotton, mordanted with tannin, a brilliant blue.

Indulines are obtained by heating aniline hydrochloride with aminoazobenzene. The following constitution has recently been established for one of the indulines:



The **Quinoxalines** contain the nucleus  ; the **Fluorindines** can be represented by the formula:



VII. ANILINE BLACK. The oxidation in various ways of aniline salts in acid solution gives aniline black, which is of considerable importance in the dyeing of cotton.

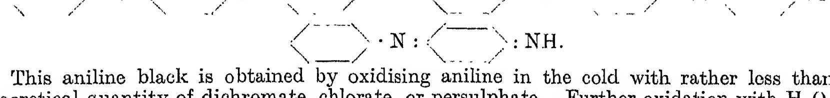
Among the different oxidising agents, a special place is occupied by vanadium salts (suggested by Witz in 1877), which bring about the oxidation of large quantities of aniline (transferring oxygen by catalytic action); 1 part of vanadium, in presence of a sufficiency of potassium chlorate, oxidises as much as 270,000 parts of aniline hydrochloride. In point of efficiency, vanadium is followed by cæsium, uranium, copper, manganese and lead, the action of iron being much less.

Aniline black has a feebly acid character and is insoluble in almost all solvents. It dissolves with difficulty in aniline and forms with it a violet and then a brown colour; phenol dissolves it more easily, giving a green coloration. With fuming H_2SO_4, it yields soluble, coloured sulpho-compounds. Acetic anhydride gives a faintly coloured acetyl-derivative, and potassium dichromate a violet-black product. When treated with permanganate and then with oxalic acid, aniline black is partially decolorised. Energetic reducing agents ($Sn + HCl$) decompose it completely.[1]

[1] The *chemical constitution of aniline black* has been the subject of much discussion. Assuming that the first intermediate product of the oxidation of aniline is aniline black (Nietzki), it cannot be true, as is often thought, that the transformation of aniline into quinone by oxidation takes place through the intermediate stages of phenylhydroxylamine and *p*-aminophenol, since these do not yield aniline black on oxidation, phenylhydroxylamine giving a nitrosobenzene and not a quinone; nor can aminodiphenylamine (Nover, 1907) be formed, since this, on oxidation, gives *emeraldine*, a compound never obtained in the oxidation of aniline. It has now been found possible to convert aniline black to the extent of 95 per cent. into quinone by oxidising with lead peroxide (chromic acid giving less than 80 per cent.), so that the indaminic formula (proposed by Bucherer, 1907) can no longer be attributed to aniline black, since, according to this, it would give only 50 per cent. of quinone. This result led R. Willstätter and S. Dorogi (1909) to suggest for aniline black the formula $(C_6H_4N : C_6H_4 \cdot NH)_4$, *i.e.*, $C_{48}H_{36}N_8$, which is confirmed by the fact that the oxidation requires $1\frac{1}{2}$ atom of oxygen per molecule of aniline with a yield of 97 per cent. Further, the determination of the molecular weight by hydrolysis of aniline black with dilute sulphuric acid at 200° indicates clearly the separation of one-eighth of the nitrogen as ammonia:

$$C_6H_4N : C_6H_4 : NH + H_2O = C_6H_4N : C_6H_4 : O + NH_3.$$

All these results point to the trebly quinonoid formula of aniline black as the most probable:



This aniline black is obtained by oxidising aniline in the cold with rather less than the theoretical quantity of dichromate, chlorate, or persulphate. Further oxidation with H_2O_2, for example, results in the elimination of 2H and the formation of a quadruply quinonoid aniline black, $C_{48}H_{34}N_8$, the base of which is very dark blue-black while the salts are dark green. It

In practice aniline black is produced directly on the fibre, and the use of this very stable colouring-matter is due especially to the studies and initiative of Prud'homme, C. Koecklin, Paraf, etc.

After many improvements, the production of aniline black (termed also *oxidation black* or *fine black*) directly on cotton fibre is now carried out as follows (the quantities given are for 50 kilos of cotton). The three following solutions are prepared separately: I. 5·5 kilos of aniline oil (*see* p. 659) + 4·25 kilos of commercial HCl + 50 litres of water; II. 3·5 kilos of sodium (or potassium) chlorate + 50 litres of water (1·5 kilo of starch is sometimes added); III. 3 kilos of potassium ferrocyanide in 20 litres of water. When cool, the solutions are mixed (1 grm. of vanadium chloride is sometimes introduced) and the yarn or fabric immersed until it is well soaked. It is then gently pressed and passed slowly over rollers through the oxidation chamber (*see illustration given later*) so that at least an hour elapses before it emerges at the opposite end. The temperature of the chamber should not exceed 50° and the humidity 25°. The fabric assumes a coarse greenish colour which is changed to a fine black when it is transferred to a *Jigger* (*see later*) containing 2 kilos of potassium dichromate, 250 grms. of sulphuric acid and 100 to 120 litres of water at the temperature 50°. The black thus obtained, when thoroughly washed, is turned green only to a slight extent in the light.

VIII. QUINOLINE AND ACRIDINE COLOURING-MATTERS. Among the quinoline dyestuffs are *quinoline yellow* (water- or alcohol-soluble), *quinoline red, cyanine*, etc.; all of them contain one or more of the chromophores, $C_6H_4\left\langle\begin{array}{l}CH = CH \\ \quad\quad | \\ N = CH\end{array}\right.$, or its homologues.

Acridine derivatives possibly contain a quinonoid chromophore of the formula

$$RC\left\langle\begin{array}{c}C_6H_3(:NH)\\ \\ C_6H_4\end{array}\right\rangle NH.$$

They are obtained by condensing *m*-diamines with formaldehyde, heating the resulting tetraminodiphenylmethane with acid to remove ammonia, and finally oxidising with ferric chloride. To this group belong *acridine orange* and *yellow, phosphine, benzoflavine*, etc.

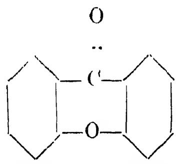
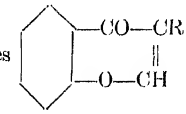
IX. THIAZOLE COLOURS. These contain the group $\begin{array}{l}=C-N \\ \;\;| \\ =C-S\end{array}\!\!\Big\rangle C-$ with the chromophore $-C = N-$ and are formed by heating *p*-toluidine with sulphur, the resulting **Primuline** being probably of the constitution

$$CH_3 \cdot C_6H_3\left\langle\begin{array}{c}N\\ \\ S\end{array}\right\rangle C \cdot C_6H_3\left\langle\begin{array}{c}N\\ \\ S\end{array}\right\rangle C \cdot C_6H_4 \cdot NH_2:$$

it may be easily sulphonated, dyes cotton directly and may be diazotised and developed on the fibre (*see* p. 781). The methyl derivative is **Thioflavine.** These colouring-matters are not very fast against light.

X. COLOURING-MATTERS OF THE OXYKETONES, XANTHONE, FLAVONE, COUMARIN. This group embraces many valuable mordant colouring-matters: *alizarin yellow, anthracene yellow, alizarin black* (*see* Alizarin Colouring-Matters, p. 783), *flavopurpurin, alizarin green, alizarin blue, alizarin cyanine, anthracene blue*, etc. The characteristic

absorbs only $2\frac{1}{2}$HCl whilst the trebly quinonoid black absorbs 4HCl; all of the latter are displaced by ammonia, which, however, in the former case, leaves 1HCl (4·5 per cent. of Cl in the nucleus). In practice the quadruply quinonoid black is obtained with excess of a slow oxidising agent acting in the cold, *e.g.*, with chlorate and copper sulphate or with chlorate and vanadium. On hydrolysis, the quadruply quinonoid black also loses one-eighth of its nitrogen as ammonia, forming the more complete black, $C_{48}H_{33}ON_7$, which is not turned green by SO_2. Oxidation of the corresponding product of hydrolysis of the trebly quinonoid black gives the same quadruply quinonoid black, $C_{48}H_{33}ON_7$. The practical preparation of aniline black in a single bath leads to the quadruply quinonoid black that turns green, and further oxidation of this in the hot yields the black which does not turn green, the terminal imino-group being hydrolysed. This latter black is obtained also by the two- (or more) bath process or by steaming. Oxidation of amino-diphenylamine instead of aniline gives first the reddish-blue imine (C_{24} . . . .), *emeraldine*, which then polymerises, forming the black (trebly quinonoid).

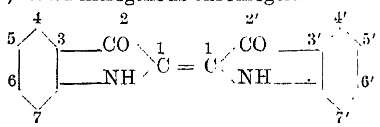
group of the xanthones is , and that of the flavones .

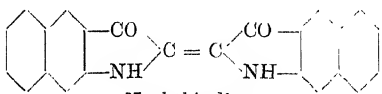
Indian yellow is a hydroxy-derivative of xanthone.

XI. INDIGO, INDIGOIDS, AND OTHER NATURAL COLOURING-MATTERS. In addition to what has been stated with reference to indigo (*see* p. 757 *et seq.*), it may be said that there are a number of derivatives of artificial indigo which are reduced with hydrosulphite and alkali and give very fast colours which are superior to indigo and resist even concentrated solutions of chloride of lime.[1]

[1] Bohn has given the name *vat dyestuffs* to those insoluble pigments the molecule of which contains at least one ketonic group capable of being reduced (*e.g.*, by hydrosulphites), taking up hydrogen and thus becoming soluble in an alkaline liquid and fixable by animal and vegetable fibres. These vat dyestuffs may be divided into two classes: *indigoids* and *indanthrene derivatives*. The first class comprises two series: *symmetrical* (indigo, etc.) and *unsymmetrical* (indirubin, etc.), and each series contains various families of the following types, to all of which the chromogen, —CO—C=C—CO, is common.

(1) With nitrogenous chromogen.

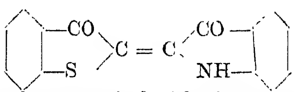




Naphthindigo

Indigo and its halogenated and other substitution derivatives: chloro-, bromo-, alkyl-, and naphthol-indigo. The substitution takes place in the benzene nucleus; many polybromo-derivatives are formed. The colours range from reddish blue to greenish blue. The *antique purple* recently studied by Friedländer is 6 : 6′-dibromoindigo. 5-Bromoindigo (*pure indigo R*), 5 : 5′-dibromo-indigo (*pure indigo 2B*), 5 : 7 : 5′-tribromoindigo (*Ciba blue B*), 5 : 7 : 5′ : 7′-tetrabromoindigo (*Ciba blue 2B* or *indigo 4B*) have been prepared.

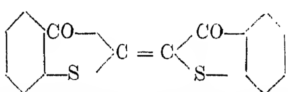
(2)



Mixed symmetrical with nitrogen and sulphur chromogens

Besides the chromophore $\genfrac{}{}{0pt}{}{CO}{NH}\!>\!C=$ of indigo, these have also the chromophore $=C\!<\!\genfrac{}{}{0pt}{}{CO}{S}$. Belonging to this family are: *Ciba grey G* (monobromo-derivatives), *Ciba violet R, B, 3R* (these are polybromo-derivatives of *Ciba violet A*).

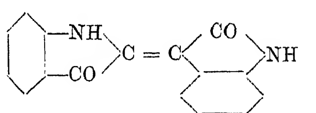
(3)



Symmetrical with sulphur chromogen

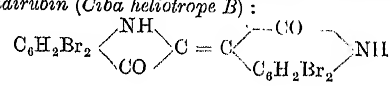
The first term is Friedländer's *thioindigo* (or *thio-indigo red B*); *Ciba bordeaux B* (5 : 5′-dibromo-thioindigo) and numerous derivatives in which the 5- and 5′-positions are occupied by alkoxy- and thioalkyl-groups have been prepared, among these being red and brown colours and the various colours of the helindone series of Meister Lucius und Brüning.

(4)

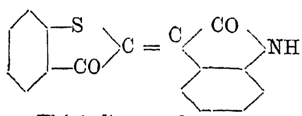


Indirubin with asymmetric nitrogen chromogen

Indirubin is not a colouring-matter, since on reduction it forms indigo, but use is made of *tetrabromo-indirubin* (*Ciba heliotrope B*):

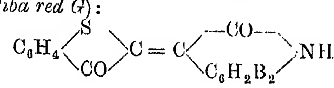


(5)

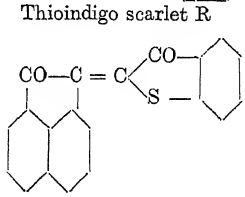


Thioindigo scarlet R

The dibromo-derivative forms *thioindigo scarlet G* (or *Ciba red G*):



(6)



is known by the name of *thioindigo scarlet 2G* (*Ciba scarlet G*).

The **Indanthrene Colours**, which were at first very expensive, are now obtainable at more reasonable prices and give medium and dark shades. They are so resistant to various reagents that they are used as pigments in place of ultramarine, etc.; they are used also for blueing sugar and other foodstuffs, as they are fast to light and non-poisonous.

Materials dyed with indanthrene dyestuffs do not stand heating in an autoclave with alkali, the colours being reduced and rendered soluble. The Badische Anilin- und Soda-

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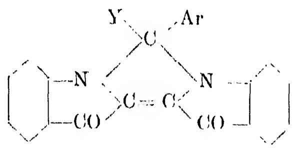
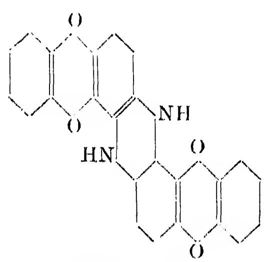
(7)



This is a new family which has given the first yellow colours of the indigoid group (*Ciba indigo yellow 3G* and *Ciba yellow G*, which is a dibromo-derivative of the preceding). The group Ar is the benzoyl residue, but it is not known whether Y is H or OH, or whether it represents a double linking to the nitrogen atom.

The second class is that of the anthracene derivatives, with the following families:

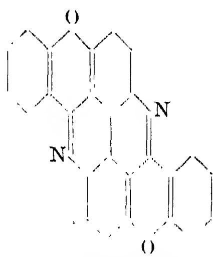
(1)



Indanthrene blue.

Indanthrene is formed by condensing 2 mols. of aminoanthraquinone by means of fused alkali and is a *dianthraquinonedihydroazine*. With reducing agents, partial reduction of the ketonic group occurs, dihydroindanthrene becoming soluble in alkali and dyeing cotton directly. The halogenated derivatives are of a more greenish-blue, resistant to oxidising agents and to chlorine. Use is made of *indanthrene blue GC, GCD, 3G*, and 3 *RC* and of *algol blue* and *algol green*. The GCD blue is obtained by boiling indanthrene with aqua regia. *Anthraflavone* (yellow) is similar to indanthrene, but without the NH groups.

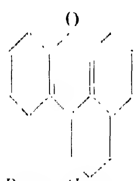
(2)



Flavanthrene

Flavanthrene (or *indanthrene yellow G* and *R*) is obtained by oxidising 2-aminoanthraquinone with antimony pentachloride in boiling nitrobenzene solution. An analogous compound which has an orange-yellow colour, and in which the two nitrogen atoms are replaced by CH, is *pyranthrene* (or *indanthrene golden orange G*), the halogen derivatives of which tend to red; of these, *dibromopyranthrene* (or *indanthrene scarlet G*) is used.

(3)



Benzanthrone

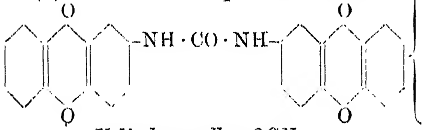
Benzanthrone is obtained by condensing anthraquinone or its derivatives with glycerol in presence of concentrated H_2SO_4. Benzanthrone and its halogen derivatives are not colouring-matters, but by various condensations they lead to excellent colouring-matters, such as *violanthrene*, the dibromo-derivative of which is *indanthrene green B*; *isoviolanthrene* (which has a similar constitution to pyranthrene) and its dichloro-derivative (*indanthrene violet RR extra*).

(4)

Anthraquinonimide derivatives

Indanthrene bordeaux B and *indanthrene red G* and *R* are formed from 3 mols. of anthraquinone joined in various ways by two imino-groups. *Algol red*, which was the first red vat dyestuff of the anthraquinone series, consists of 2 mols. of anthraquinone united by an NH group, one of them being condensed with a pyridone ring.

(5) *Aciaminoanthraquinone* derivatives



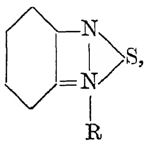
Helindone yellow 3GN

Characteristic of these is the complex of several NH groups united once or more times to CO groups. *Helindone yellow 3G* represents two anthraquinone groups condensed with urea. Various other condensations of aminoanthraquinones with benzoyl, succinic, tartaric, phthalic, etc., groups give *algol reds G, R*, and *5G*, etc.

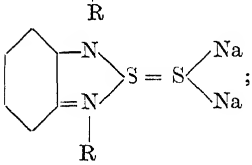
Fabrik recommend the addition of an oxidising agent to the autoclave bath to prevent the reduction.

XII. SULPHUR COLOURING-MATTERS. These colouring-matters, which have been discovered since 1893, are very fast on cotton, which they dye directly without a mordant, but in alkaline and reducing solution (sodium sulphide and sometimes a little glucose) which prevents any unevenness which might be produced in the colouring owing to contact with the air. The sulphur colouring-matters do not dye wool or silk in presence of sodium silicate (or of blood or diastofor), so that two colours can be obtained on wool and cotton fabrics, the wool being dyed first with an acid dyestuff and the cotton subsequently with a sulphur colouring-matter in a bath of sodium sulphide and silicate (or blood or diastofor).

They are obtained by melting together sulphur or sodium sulphide and various other colouring-matters or other organic compounds. *Cachou de Laval* has been known since 1873 but has been used but little. It was obtained by Croissant and Bretonnière by fusing sawdust, bran, or the like with sodium sulphide. In 1893 the discovery of *Vidal black* directed the attention of manufacturers to this interesting group of colouring-matters, which now include almost all tints except red, and are obtained by fusing with sulphur or sodium sulphide, derivatives of benzene, naphthalene, diphenylamine, anthraquinone, etc. These colouring-matters are placed on the market by various firms under different names, although their compositions are practically the same: the firm of Cassella calls them *immedial colours*; the Bayer Company, *katigenic colours*; the Badische Company, *kriogenic colours*; the Berlin Aktien-Gesellschaft, *sulphur colouring-matters*, etc. The constitution of these colours has not been firmly established, but during recent years a little light has been thrown on them. According to Sandmeyer (1901) they are derivatives of Piazthiol



, the compound soluble in sodium sulphide having the constitution



; but nowadays other interpretations have been given.

When diphenylamine-derivatives are fused with Na_2S, black colouring-matters are preferably formed, with aminohydroxydiphenylamine derivatives and the corresponding N-alkyl and N-aryl compounds blue colours are obtained, while in presence of stable meta-substituted compounds, brown or yellow colouring-matters are formed.

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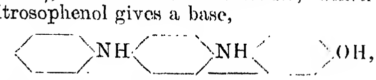
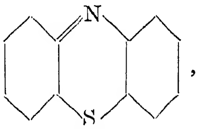
(6) Various types: *Rufanthrene, leucol, cibanones, hydrones, indigolignoids* — These colouring-matters are obtained by fusing aminoanthraquinones with sulphur or alkaline sulphides (*rufanthrene* browns, greys, olives), *e.g.*, *indanthrene brown*, *cibanone brown*, *cibanone yellow*; the first *cibanone black* was obtained from methylbenzanthrene, and the *leucol* colours of the firm of Bayer are also of this group. A mixed indigoid-anthracene group has also been obtained. Thus, the action of isatin chloride, etc., on α-naphthol (or its ortho-derivatives) gives the indigoid colouring-matter and an isomeride of analogous properties, *e.g.*, *indonaphthalene* or *indolignone* (Friedländer and Bezdzich, 1909); both the indigoid and the indolignone are decomposed by alkali into anthranilic acid and the corresponding hydroxynaphthaldehyde. A group of sulphur vat dyestuffs is that of the *indrone blues* (Cassella), derived from carbazole, which with *p*-nitrosophenol gives a base,

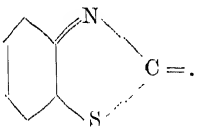


and this, when fused with sulphur or sulphides forms reducible colouring-matters soluble in alkali.

In general the reaction takes place with preliminary formation of aromatic mercaptans or polymercaptans (in the ortho-position with respect to N or to O), which give further condensation products, *e.g.*, black derivatives of thiodiphenylamine (of *thiazine*),



and yellow or brown colouring-matters derived from thiazole (*see above*),



They form insoluble condensed products (disulphides) with the oxygen of the air, these being rendered soluble again by alkaline reducing agents (sodium sulphide, hydrosulphites, etc.). The fixation and development of the colour in the cotton fibres consist simply in the oxidation of the mercaptan to disulphide. The black or blue sulphur colouring matters are quinonimino-derivatives of the thiazine group. These colouring-matters are now used in large quantities, the production of *sulphur black* alone in 1909 being estimated at nearly 5,000,000 kilos. It has been proposed (1909) to render them faster to washing by treatment with formaldehyde or by immersion in a nickel sulphate bath.

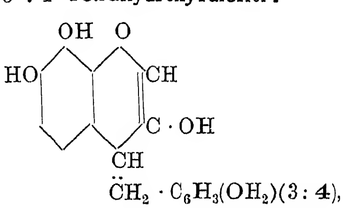
The principal natural *mordant* colouring-matters are: logwood, brazilein, archil, cochineal, catechu, sandalwood, etc.; and the natural *substantive* dyes for cotton and wool are: bixin, curcumin, carthamin, etc.

These dyewoods are placed on the market in small trunks or in chips; for economy in transport and convenience in use, dense aqueous or concentrated dry extracts are often prepared.

LOGWOOD or **Campeachy** is obtained from the barked trunk of a tree (*Hæmatoxylon campechianum;* Fig. 471 shows twig, leaves, flowers, and seeds) which grows in Central America and in the Antilles, the best qualities being those of Honduras, San Domingo, and Jamaica. Just as the consumption of indigo has not diminished in spite of the competition of the numerous artificial aniline and alizarin colours, so also the use of logwood in dyeing tends to increase, although not in similar proportion to the artificial dyes. The wood arrives in Europe in logs weighing 150 to 200 kilos, which are sawn into short pieces, chopped and reduced to chips or raspings; more rarely they are ground.

The colouring-matter of logwood was studied by Chevreul in 1810, by Erdmann in 1842, and by Hess and Reim in 1871. It consists of a glucoside which occurs in the *fresh* wood and which, perhaps by simple fermentation or by the action of water and air, separates the base of the colouring-matter, *i.e.*, **Hæmatoxylin**, $C_{16}H_9O(OH)_5$, and this, under the influence of atmospheric oxygen (best in presence of alkali), gives the colouring-matter *hæmatein* (which dyes with metallic oxides), $C_{16}H_{12}O_6$, 2H being thus lost. Hæmatein is moderately soluble in water, alcohol, ether, or glacial acetic acid, and insoluble in chloroform or benzene. In ammoniacal solution it assumes a purple-red colour, which becomes brown in the air. By reducing agents (H_2S, SO_2, Zn + HCl, etc.) hæmatein is decolorised without, however, giving hæmatoxylin.

Hæmatoxylin is probably 3 : 4 : 3′ : 4′-**Tetrahydroxyrufenol**:



and hæmatein would have a quinonoid formation in place of the hydroxyl of the first nucleus, H being lost together with another H from the para-CH of the second nucleus.

In dyeing, logwood is used in chips or as an extract. The chips are first matured (? fermented) by moistening with water, heaping up and stirring every two or three days for one or two weeks, care being taken to prevent heating of the mass, which would destroy the colouring-matter. The wood changes from a yellowish to a brownish red colour and is extracted with boiling water, to which it gives up 2·5 to 3 per cent. of its weight. The

solution, which is rich in hæmatein, is used as it is in the dye-vat, whereas logwood extracts are prepared in the way used to obtain tanning extracts (p. 691); these extracts are very rich in hæmatoxylin. *Solid hæmatein*, a pure, granular product, free from tannins, is obtained by direct extraction of the ground logwood with ether.

Hæmatein is a mordant colouring-matter, *i.e.*, is fixed and gives intense and fast colours only on mordanted fibres,.and is generally used for black or blue-black shades with various shot effects, according to the nature of the mordant: with aluminium salts it gives a greyish violet-black, with chromium salts blue-black, with iron salts grey-black, with copper salts greenish blue-black, and with tin salts violet-black.

A fine black is usually obtained by mordanting, *e.g.*, wool, for 2 hours in a boiling bath containing 2 to 3 per cent. of potassium dichromate, 3 to 4 per cent. of tartar (or 2 per cent. sulphuric acid, 3 per cent. lactic acid, etc.) and 0·5 to 1 per cent. of copper sulphate (all calculated on the weight of fabric). The mordanted fabric is well washed and dyed in a boiling aqueous bath, to which is added the dilute logwood extract or 5 to 8 per cent. of the concentrated extract or the matured chips in bags. To obtain black-black (coal-black without blue reflection), 0·2 to 0·5 to 1 per cent. of Cuba yellow wood extract is added. Dyeing is followed by thorough washing in cold water.

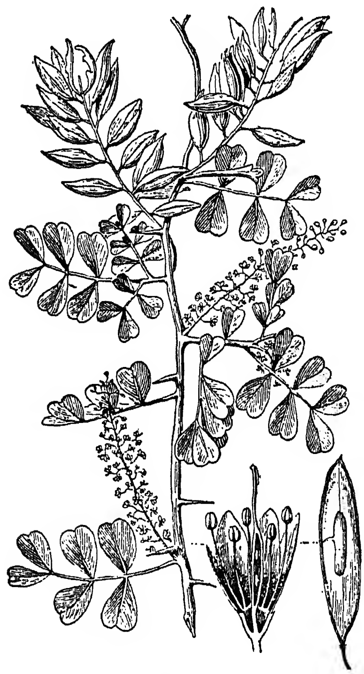


Fig. 471.

Cotton is first mordanted in the usual way in a tannin bath (2° to 3° Bé. overnight), then passed into an iron nitrate bath (*see* Dyeing of Silk, *and note on* p. 771), rinsed and dyed in the hot aqueous bath with logwood and yellow wood. After dyeing the bronze-red appearance is removed by a soap bath.

For dyeing silk black, *see later.*

Logwood extracts are often adulterated with chestnut-bark extract, molasses, dextrin, sumac, etc., and as a rule the best test consists in dyeing equal weights of mordanted fabric with equal weights of the suspected and a pure extract. Sugar (molasses) or dextrin may be detected by precipitating with a slight excess of lead acetate and examining the filtrate by means of either Fehling's solution or the polarimeter.

Chestnut-bark extract is detected by treating 1 grm. of the extract, dried at 100°, with ether and weighing the portion dissolved by the ether. The residue is then extracted with absolute alcohol and the amount dissolved determined. A good, dried extract contains 86 to 88 per cent. of matter soluble in ether and 12 to 14 per cent. soluble in alcohol, while, if chestnut-bark extract is present, less dissolves in ether and more in alcohol.

ARCHIL is extracted from *Roccella tinctoria* (2 to 12 per cent.) or from other lichens growing on the coast or on bare rocks in mountainous districts. The red colouring-matter is formed after fermentation in presence of a little ammonia, and after the action of atmospheric oxygen. Prior to fermentation, the colourless compounds contain roccellic acid (p. 365) and erythric acid, while, after the decomposition, orcin (*see* p. 645) is present; the latter, when oxidised in presence of NH_3, gives orceine (*see* p. 645), which forms violet-red lakes. Archil is placed on the market as extract or solid preparation.

Cudbear (or *perseo*) is obtained from *Lecanora tartarea* and dyes wool and silk very uniformly in presence of alum, tin salt, and tartaric acid.

Litmus (or *tournesol*) is formed from orcin by the action of ammonia or soda, and is obtained from various lichens (*Roccella tinctoria*). The extract is mixed with gypsum or chalk and made into tablets, which contain various colouring-matters (*azolitmin, erythrolein, erythrolitmin, spaniolitmin*). It is very sensitive to acids, which redden it, and to alkalis, which turn it blue, and hence serves as an excellent indicator.

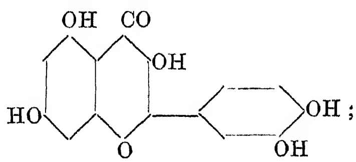
COCHINEAL has been long used as a colouring-matter and is the female of the insect *Coccus cacti*, which lives on the cactus of the Canary Islands, Algeria, Java, Guatemala, etc.

When the insect is three months old (weight = 0·0065 grm.) it is killed with hot water (*black grain*) or in an oven (*silver grain*). The colouring-matter is **Carminic Acid**, $C_{17}H_{16}O_{10}$. The dry insects are powdered and extracted several times with boiling water, the dye-bath being prepared with hot water, 3 per cent. of oxalic acid and 0·5 per cent. of tin salt; the wool is immersed in this for at least 30 minutes at a boiling temperature. The wool may be first mordanted separately with oxalic acid and tin salt and then dyed in the aqueous cochineal.

YELLOW WOOD or **Cuba Wood** (*Old fustic*) is obtained from the trunks of *Morus tinctoria* or of *Maclura tinctoria* of the West Indies, Brazil, and Mexico, the best kinds being, however, those of Cuba, Tampico, Porto Rico, and Jamaica. The colour may be extracted from the wood by means of steam, and the concentrated extract contains a tanning material (*maclurin*), since a brighter yellow is obtained on dyeing if a little gelatine is added to precipitate this tanning substance; if this is not done, prolonged boiling gives dark or brownish shades. Although *Cuba yellow* dyes pure fibres directly, really fast colours are obtained only by chrome mordanting, etc.; hence Cuba yellow is used together with logwood or even alizarin or anthracene colouring-matters.

QUERCITRON is sold in small chips or, better, as a coarse powder obtained by grinding the bark—freed from epidermis—of *Quercus tinctoria* and *Q. nigra*, which grow in Pennsylvania, Carolina, Scotland, France, and the South of Germany.

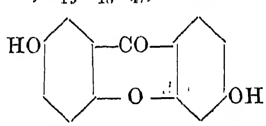
The dilute aqueous extract does not keep, and must hence be used immediately. Chevreul separated from the bark the compound **Quercitrin**, $C_{21}H_{22}O_{11} + 2H_2O$, which when boiled with acid takes up 1 mol. H_2O, giving **Quercetin**, $C_{15}H_{10}O_7$, and **Isodulcitol**, $C_6H_{14}O_6$. Quercetin is **1 : 3 : 3′ : 4′-Tetrahydroxyflavanol**



it dissolves in alkali, giving an orange-yellow coloration, and yields phloroglucinol and protocatechuic acid when fused with alkali. It is sulphonated by concentrated sulphuric acid, forming a direct dye for wool.

It dyes more especially animal fibres (wool) either previously mordanted or with an alum or chrome mordant added to the dye-bath. Similar behaviour is shown by *flavin*, which is a more concentrated preparation of quercitron and contains quercetrin and quercetin.

Natural **INDIAN YELLOW** is still extracted in Bengal from the evaporated residue of the urine of cows fed on mango leaves. It contains a hydroxyl derivative of *xanthone*, namely, **Euxanthone**, as glycuronic ester (*euxanthinic acid*, $C_{19}H_{18}O_4$), which is decomposed by hot hydrochloric acid into **Euxanthine**, $C_{13}H_8O_4$ or



(obtained synthetically by condensing hydroquinonecarboxylic acid with β-resorcylic acid).

Natural Indian yellow functions as a mordant dyestuff, but is now scarcely used for textiles, as it is not very stable to light.

BRAZIL WOOD or **Red Wood** is obtained from the trunk of *Cæsalpina brasiliensis* and other varieties. The colourless glucoside it contains gives, on fermentation or when treated with acids, glucose and **Brazilin**, $C_{16}H_{14}O_5$ or $C_6H_3(OH)_2 \cdot C_4H_4O \cdot C_6H_5O_2$, which is coloured carmine by alkali and decolorised by acids or reducing agents; it gives intensely coloured lakes and oxidises in the air, forming **Brazilein**, $C_{16}H_{12}O_5$, while with concentrated nitric acid it gives trinitroresorcinol and, when fused with alkali, resorcinol. It is a red mordant (alum or chrome) colouring-matter, but is only slightly fast to light.

Brazilin seems to have a constitution analogous to that of hæmatoxylin (*see* p. 791) with a hydroxyl group less in the first benzene nucleus, brazilein being apparently the corresponding quinonoid derivative similar to hæmatein (*see above*).

SANDALWOOD is the wood of *Pterocarpus santalinus*, which grows in Madagascar, tropical Asia, and Ceylon. **Santalin** or **Santalic Acid**, $C_{17}H_{16}O_6$, which forms the colouring-

matter of this wood, occurs in abundance in other plants (in *barwood* or *Baphia nitida* of Sierra Leone and in *camwood* or *kambewood* from West Africa).

Santalin gives resorcinol, acetic acid, etc., when fused with alkali, but its constitution is not yet established. It is a mordant colouring-matter, like logwood, and was once used with alizarin to dye cotton red.

CATECHU (or **Cutch**) and **GAMBIER** are extracted from various plants of India, Bengal, Malay, etc. (palm, mimosa, Rubiaceæ, *Acacia catechu*, *Areca catechu*, *Uncaria gambier*, etc.). They contain tannin and colourless catechol, partly combined to a brown colouring-matter. When fused with alkali, they give phloroglucinol, pyrocatechol, and protocatechuic acid. With various mordants they give stable browns or olives, which do not, however, withstand chlorine or acid. On cotton they give reddish or yellowish brown colours which become fast to light after treatment with alkali dichromate at 60° to 70° (*khaki* used for uniforms in the British, German, and Italian armies).

Nowadays a much faster khaki is obtained by impregnating the white fabric in a cold concentrated bath of pyrolignite of iron, chromium acetate, and a very small proportion of manganese chloride, drying it thoroughly, immersing it in a boiling bath of caustic soda (11° Bé.) and a little sulphoricinate, and oxidising in a hot-air chamber or by means of dichromate solution. With a less concentrated soda bath or one not boiling, the metallic oxides would be precipitated superficially on the fibre, and the dry fabric would be dusty and would wear out sewing needles.

This khaki is very fast against light, scouring, and chlorine, but does not *resist perspiration* (test with a mixture at 1° Bé. of hydrochloric, formic, and acetic acids for 5 hours). *Fastness to perspiration* is given by boiling the dyed fabric for 2 hours in a silicate bath at 6° to 7° Bé.

CHLOROPHYLL is not a colouring-matter for textiles but is the green pigment which occurs in many plants (those which assimilate CO_2) and brings about the transformation of the carbon dioxide into starch in the leaves under the action of sunlight—especially of certain rays of the spectrum—and apparently also with the help of an enzyme (Willstätter and Stoll, 1911) known as **Chlorophyllase**. With starch, wax, etc., it forms the characteristic chlorophyll granules of green leaves (*see* p. 525).

It is soluble in oil, alcohol, ether, or chloroform, its solutions showing blood-red fluorescence and readily undergoing change. Its constitution is still uncertain, and it does not appear to contain combined iron, as was formerly thought. Following the indications of the botanists Borodin (1882) and Monteverde (1893), Willstätter and Benz (1908) obtained a pure chlorophyll[1] (2 grms. from 1 kilo of dried leaves) in dark, bluish black crystals with a metallic lustre, which are insoluble in petroleum ether but soluble in alcohol or ether, giving a bluish fluorescence. The green solution of this product, which exhibits the same spectrum as the chlorophyll of fresh leaves, is turned brown by alkali, but again becomes green. Its formula is probably $C_{55}H_{72}O_6N_4Mg$, and the magnesium present (3 per cent.) is perhaps the cause of the catalytic action effecting the transformation of CO_2 into starch; it does not contain phosphorus, as many, including Stoklasa, have thought. Acids remove all the magnesium, the residue being **Phœophytin**, which is similar to chlorophyll, is ethereal in character, and forms various products (*e.g.*, *methyl alcohol, phytol, phytochlorin,* and *phytorodin*, which has the formula, $C_{34}H_{34}O_7N_4$, is acid in character and contains four pyrrole groups) and three carboxyl groups when hydrolysed with alkali.

Phytol forms one-third by weight of the chlorophyll of plants and is a primary, unsaturated, monohydric alcohol, $C_{20}H_{40}O$, capable of combining with Br_2. Plants produce also an amorphous chlorophyll which, unlike the other, gives phytol on hydrolysis. It is thought that it is analogous in chemical composition to the colouring-matter of the blood (*see later*), since both yield pyrrole when distilled with zinc dust. Willstätter and Isler (1911) showed that chlorophyll contains two colouring-matters: (*a*) bluish green and (*b*) greyish black (one-fourth as much as of the first), having the formula, $C_{55}H_{70}O_6N_4Mg$, thus confirming the hypotheses of Stokes (1867 and 1873) and of Tswett (1906); the two colours are separated

[1] As chlorophyll readily undergoes change, it is extracted in the cold with methyl alcohol from the carefully dried, powdered leaves (Willstätter), previously washed with petroleum ether. In order to separate it from other colouring impurities, its alcoholic extract is suitably diluted and extracted with ether (benzene or carbon disulphide), many of the impurities remaining dissolved in the alcohol; or the alcoholic extract may be shaken with a large amount of water, which dissolves the chlorophyll in the colloidal state, the decanted aqueous solution being treated with salt and extracted with petroleum ether containing a little alcohol. From this solution the chlorophyll is deposited pure if the whole of the alcohol is eliminated by washing.

by more or less dilute alcohol. Chlorophyll is used in practice to colour oils, soaps, fats, preserved vegetables, etc.; before the war it cost 8*s.* per kilo or, for the highly purified product, 80*s.* per kilo.

TESTING OF COLOURING-MATTERS

Out of the thousands of colouring-matters sold by different firms under most varied and fanciful names, the majority represent, not chemical individuals, but intimate mixtures of several colours which give directly the tints desired.

The colouring-matters obtained at the end of the manufacture by precipitation or separation from their solutions by means of salt (just as with soap) are not sold in the pure state, but are diluted with 50 per cent. or 75 per cent. of finely ground sodium chloride or sulphate. A *mixture* may be distinguished from a chemical individual by the following simple test: a few milligrams are blown in a cloud from a watch-glass and are caught on a moist filter-paper spread on a sheet of glass at a short distance from the watch-glass. If the filter-paper were not too moist, it shows on drying isolated, swollen points of colour, the uniformity or non-uniformity of which is readily seen. A variation of this test consists in sprinkling a little of the powder on to the surface of concentrated sulphuric acid contained in a flat porcelain capsule.

The use of the *spectroscope* has been suggested for differentiating between various groups of colouring-matters, the positions of the absorption bands being observed when white light is passed through an aqueous or alcoholic solution of the colouring-matter of definite concentration contained in a glass vessel with parallel glass walls. The spectroscope is now, however, scarcely ever used, owing to the uncertainty of the results obtained, but it is useful in detecting the colouring-matter of the blood (*see later* Hæmoglobin).

The qualitative analysis of colouring-matters for the detection of the principal groups may be carried out according to the method of A. G. Roto [1] or to those of Weingärtner and Green. The latter, which are largely used, are briefly as follow:

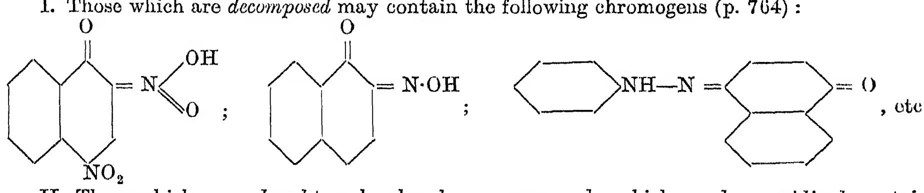
I. COLOURING-MATTERS SOLUBLE IN WATER. (*A*) If the aqueous solution gives

[1] Rota's method, extended by Buzzi (1911), for analysing colouring-matters consists of four series of tests:

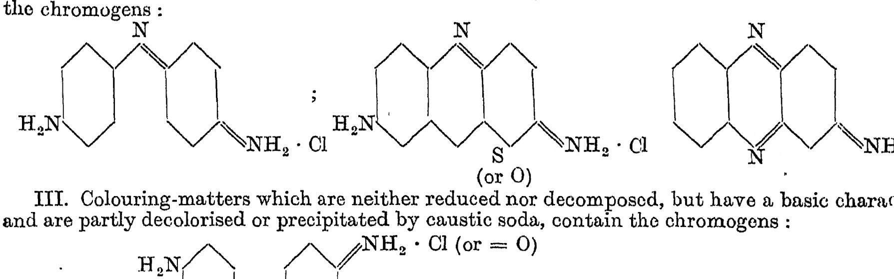
A. This is based on the usually quinonoid character of these matters and hence on their behaviour towards acid reducing agents, preferably stannous chloride; the alkaline reducing agents do not serve well, as with all colouring-matters they give leuco-derivatives which are not very characteristic.

The behaviour with $SnCl_2 + HCl$ permits of the division of all colouring-matters into the following four groups:

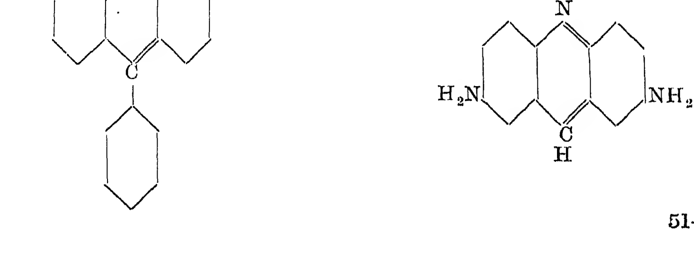
I. Those which are *decomposed* may contain the following chromogens (p. 764):



II. Those which are *reduced* to colourless leuco-compounds, which can be *reoxidised*, contain the chromogens:



III. Colouring-matters which are neither reduced nor decomposed, but have a basic character and are partly decolorised or precipitated by caustic soda, contain the chromogens:



a precipitate with a solution containing 10 per cent. of tannin and 10 per cent. of sodium acetate, the presence of *basic colouring-matters* is denoted:

(1) If the solution of the colouring-matter is reduced with zinc dust and dilute hydrochloric acid, a few drops of the decolorised solution are placed on a piece of filter-paper:

(1*a*) The reappearance of the original colour of the substance when the paper is waved

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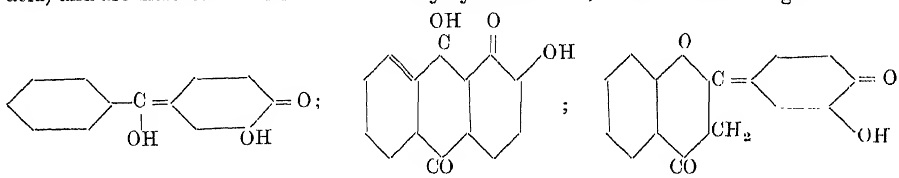
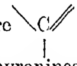
IV. Those which are neither reduced nor decomposed, and have a phenolic character (feebly acid) and are increased in colour and solubility by caustic soda, contain the chromogens:



Groups III and IV always contain the chromophore  and to these belong the acridines, the thiazoles, the auramines, the rosanilines, the pyronines, the rosamines, the phthaleins, the rhodamines, the hydroxyacetones, the hydroxyanthraquinones, the coumarins, flavone, flavonal, etc.

B. To distinguish between the different chromogens of the separate groups, other special reactions are used, for instance:

The *acridines*, with concentrated sulphuric acid, give a fluorescence resembling that of petroleum.

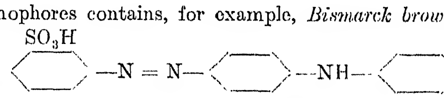
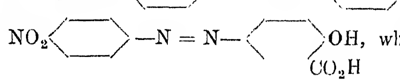
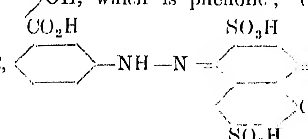
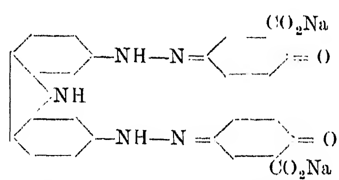
The *azo*-dyestuffs, with concentrated nitric acid, regenerate the respective diazo-salts.

The *hydroxyacetonic*, *hydroxyquinonic*, etc., colouring-matters are precipitated as lakes by stannous chloride and subsequent treatment with sodium acetate.

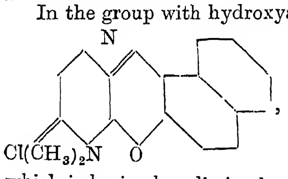
The transformation of azo- colouring-matters and their derivatives into thiazole (polychromin).

The conversion, by special reagents, of one colouring-matter into another, *e.g.*, gallein into cœrulein.

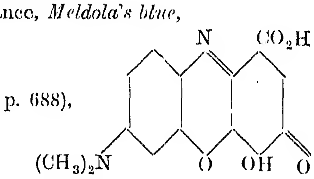
C. After the restriction of the colouring-matter to one of the four groups and after the various tests for defining more exactly the character of the chromophore have been carried out, the process of identification is continued by means of systematic dyeing tests which vary with the auxochromes and salt-forming groups (*see* p. 766), imparting to the colouring-matter a basic, acid, phenolic, substantive, or a mixed character, such as basic phenolic, acid phenolic, substantive basic, substantive phenolic.

The group with azo-chromophores contains, for example, *Bismarck brown*, which is basic (*see* p. 662); *metanil yellow*, , which is acid; *alizarin yellow R*, , which is phenolic; *Congo red* (*see* p. 781), which is substantive; *chromotrope 2R*, , which is acid phenolic; *carbazole yellow*, , which is substantive-phenolic in character.

In the group with hydroxyazine chromophores are, for instance, *Meldola's blue*,



which is basic; *gallocyanine* (*see* p. 688),



which is basic-phenolic in character.

So, also, the thiazine group (*see* p. 785) contains *methylene blue*, which is basic, and *thiocarmine*, which is acid.

The dyeing tests are made in hot neutral and acid baths, in each of which four samples are mmersed, namely, cotton, cotton mordanted with tannin, wool, and wool mordanted with

in the air indicates azines, oxazines, thiazines, and acridines, *i.e.*, according to the colour, pyronine, safranine, rosinduline, phosphine, benzoflavine, induline, etc.

(1*b*) If the original colour appears but weakly or not at all, but is formed immediately on moistening with a drop of 1 per cent. chromic acid solution, the colouring-matter belongs to the rhodamines or to the triphenylmethane group ;

(1*c*) The non-appearance of the original colour under any conditions indicates auramine, thioflavine, chrysoidine, Janos colours, Bismarck brown.

B. Non-precipitation of the solution by tannin, etc. (*see above*), denotes the presence of *acid colouring-matters* :

(2) The solution of the colour is reduced as in (1) or with $Zn + NH_3$ and a drop placed on a strip of paper :

(2*a*) The reappearance of the original colour on shaking the paper in the air indicates sulphonic or mordant dyes of the groups of azines, oxazines, thiazines, soluble induline, nigrosines or azocarmine, thiocarmine, indigo-carmine, gallocyanine, Mikado orange.

(2*b*) If the coloration reappears only after treatment with chromic acid or ammonia vapour, the original aqueous solution is acidified with sulphuric acid and shaken with ether ; coloration of the ether and complete or almost complete decolorisation of the solution indicates phthaleins or auramines, while non-coloration of the ether shows triphenylmethane dyes.

(2*c*) Non-coloration of the paper even when heated in a flame or treated with ammonia vapour points to azo-, nitro-, nitroso-, or hydrazine-colours, which, when burnt in powder

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dichromate (for the mordanting, *see* p. 771 and *later*, Dyeing Tests). The more or less intense colours assumed by the samples give indications concerning the character of the colouring-matter (*see* p. 772), and confirmation of this is obtained by various tests on the dyed fabric :

(*a*) The *colour is substantive* if, when the dyed sample of natural wool is heated in faintly alkaline water, the colour passes to the white cotton placed in the same bath ;

(*b*) The *colour is acid* if the change indicated in (*a*) is not observed, and if, when the bath is acidified, the wool takes up the colour it gave to the alkaline bath ;

(*c*) The *colour is basic* if in bath (*a*) the colour passes from the wool to a sample of white cotton mordanted with tannin ;

(*d*) The *colour is phenolic* if the tint on mordanted wool varies with the nature of the mordant.

Tests may also be made on the solution of the colouring-matter ; thus, if it is precipitated by tannin or picric acid, the *colour is basic* ; if ether extracts the colouring-matter in an acid medium, the *colour is phenolic*, whereas if ether extracts the coloured base in an alkaline medium, the *colour is basic*.

If it is established that the colouring-matter, containing a given chromophore, is basic in nature, all acid, substantive, phenolic, etc., colouring-matters with the same chromophore are excluded.

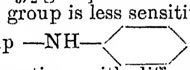
D. For the further individualisation of the colouring-matter, useful information is given by the following reactions characteristic of the substituent radicals.

The NH_2 group is recognised by diazotising and then coupling (*see* p. 782), by which means a new azo-colouring-matter is formed, or by boiling the diazotised product with water, the formation of the OH group being shown by the increased solubility in NaOH compared with that of the original colour.

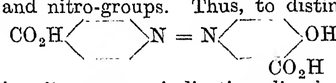
The more or less basic groups are indicated by the greater or less sensitiveness of the solution to mineral acids :

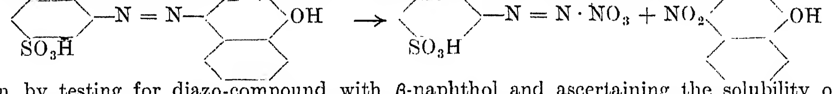
The $N(CH_3)_2$ group is sensitive, as seen in methyl violet and methyl orange ;

The NH_2 group is less sensitive, as in fuchsine and acid yellow ;

The group  is less sensitive still, as in aniline blue and metanil yellow.

Different colorations with different concentrations of acid indicate several salt-forming groups.

To complete the characterisation of a colouring-matter, the latter must be tested for halogens and nitro-groups. Thus, to distinguish alizarin yellow R (*see above*) from *diamond yellow G*, , the nitro-group is tested for by reduction and diazotisation, its presence indicating alizarin yellow. Other colouring-matters are differentiated by testing for chlorine and bromine. The *azo-dyestuffs* are characterised also by the formation of the corresponding diazonium nitrates when treated with concentrated nitric acid :



then, by testing for diazo-compound with β-naphthol and ascertaining the solubility of the nitro-derivative, the position of the sulphonic group in the molecule may be determined.

The Tables given on pp. 798–802 afford considerable help in the rapid characterisation of colouring-matters.

Recognition of the Principal Dyes on Fibres

Name of Colouring-Matter	Conc. H_2SO_4	10 per cent. H_2SO_4	Conc. HCl	HNO_3 (sp. gr. 1·40) on F [1]	10 per cent. NaOH	$SnCl_2$ + HCl
Blacks and Violets on Wool and Silk						
Indigo	F = Gn, with aq. = B s = Y, then Gn, then B	un.	un.	Y, rim Gn	un.	F = in hot somewhat D s = Gn − Y
Logwood (M. cr.)	F = Gn Br s = Y	V	R V	O and rim R	V	V then Br
„ (M. fe.)	„	„	„	Y O	„	„
Alizarin black (M. cr.)	F = almost un. s = Gr	—	F = almost un. s = r − Gr	Gn Br	+ Gn B	Gn Br
Gallocyanine (M. cr.)	s = + B, with aq. = r	s = − V	F = V, s = V	R Br	F = V Gr	—
Alizarin blue S (M. cr.)	F = GnB s = + Gn B	un.	F = r B s = r	Y and rim V	F = B − Gn s = un.	V − Gr
Alizarin cyanide R (M. cr.)	F = + R B s = + B, with aq. V	+	F = + R s = − B	Gn Gr	+ Gn	+ Br
Alizarin cyanine brill. 3 G (M. cr.)	F = +Gn, with aq. r B s = r V	—				
Acid azo-black 3 BL (M. cr.)	RV	un	F = − Bl − r s = r	Bl B	B	− Gn
„ „ „ (without M.)	R	− r	R Br	+ R Br	+ R V	D
Naphthol black B or 3 B	F = + Gn B s = B Gn, with aq. V	almost un.	F = almost un. s = un.	R − O	almost un.	R − V
Naphthylamine black D	s = Bl B, with aq. R V	„	F = almost un.	Br	s = B	almost un.
Anthracene black D	F = Bl V s = Gn Gr	„	s = − Gn F = V	Y Gn, with Br rim	s = + r	+ V R
Wool black	s = + B, with aq. V	—	F = Br V s = Br	Y with rim R	F = ÷ V	Br Gn, then D
Victoria violet 4 B S	F = B V s = V	+ R	F = R V s = r	R − O	F = Br R s = in hot D	—
Acid violet 2 B	F = Y Gr s = Y	Y Gn	F = Y Gn	Y with rim B Gn	F = almost D	+ B
Acid violet 4 B N	F = Gr s = Y	÷ R V	Y	Y with rim − Gn	F = D	Gn B
Formyl violet 4 S B	F = Gr s = Y	÷ B	F = Gr S = − Y	Y	almost D	Gn
Fast acid violet 10 B	F = Gn s = Y Gr	Gn B	F = Gn, then Y s = Y Gr	Gn, with rim Y Gn		—
Alkali violet	F = O s = Y	Gn B	F = O s = Y	Y	F = D	Gn B
Violamine R	F = R s = R Gr	—	F = ÷ B s = r	R − Y Gr	F = R	+ B
Yellow Colours on Wool						
Yellow wood	F = ÷ Y to Br R s = Y	almost un.	÷ Y	÷ Br	F = ÷ Y s = − Y	+ Y
Alizarin yellow A (M. cr.)	F = ÷ Y, s = − Y	—	F = almost un.	Y Gn	F = ÷ Y	—

Anthracene yellow (M. cr.)	F = Br, s = Br Gr	÷ Y Br	÷ R V	O, rim R V	F = ÷ Y	—
Alizarin orange (M. cr.)	F = ÷ O, s = — Br	F = almost un., s = ÷ O	F = — O, s = Y	Y Gr	F = Y O R	almost un.
Picric acid	F = Y Gr, with aq. = Y s = with aq. — Y	F = almost un. s = — Y	F = D	Y	F = O s = Y	— Y
Naphthol yellow S	F = — Br, s = D	— Y	F = D	— Br	F = almost un., s = Y	D
Azoflavine	F = V R	÷ Y	F = V R, s = R V	R, rim R V	F = ÷ Gn	— Y
Tropæolin O O	F = ÷ V B, s = V	÷ Br	F = ÷ V R, s = ÷ V R	R, rim Br	F = ÷ Y	÷ Y
Orange II	F = R Y, then R; s = R Y	—	F = R Y, then R; s = r	Y, rim R Y	F = ÷ R Y	—
Croceine orange	F = YO, s = R	÷ O	F = R, s = R	—	F = Br	D
Tartrazin	F = ÷ Y, s = Y	un.	F = ÷ Y, s = Y	O	F = Y R, s = Y	— Y then D
Milling yellow O	F = R, with aq. = Y s = R B	÷ Y	F = R s = R	R, rim Br	—	D
Quinoline yellow	F = — YR, s = — Y	—	F = ÷ Y, s = — Y	—	F = — Y	÷ Y
Thioflavine S	F = Br, then D	— Y	F = D	—	F = — Y, then D	÷ Y
Green Colours on Wool						
Alizarin green (M. cr.)	F = ÷ B, s = B	÷ B	F = B R, s = r	Br, rim R	F = ÷ Gn	Gr
Diamond green (M. cr.)	F = ÷ Gn B, s = B Gn	÷ Gn	F = Gn B, s = — Y	R, rim Gn	F = un.	almost un.
Janos green C G	Gn Gr	un.	Gn	Gn B	B	Gn Y
Fast green for wool	F = YGr	—	F = ÷ Y	Y Gn	F = ÷ Gn	— Y
Malachite green	F = Y, with aq. = Gn s = Y	÷ Y	F = ÷ O, with aq. = ÷ Gn, s = Y	R	F = D	—
Brilliant green	F = R, with aq. = Gn s = R	— Gn	F = ÷ Y, with aq. = Gn s = Y	R Y	F = D	÷ Y
Alizarin cyanine green E	Gr Gn	un.	Gr	Y Gr	almost un.	F = — Gn, s = — Y
Dark alizarin green W (M. cr.)	F = almost un., s = r	un.	F = almost un., s = r	Br	B	Br Y
Red Colours on Wool.						
Brazil (red) wood (M. al.)	F = — Br R, s = Br	slowly = R	F = ÷ R, s = R	Y, rim R	F = — R, s = R	F = R Y in hot, s = R
Sandalwood (M. cr.)	F = Br, s = Br	un.	F = Br	Br Gn	F = ÷ Br, s = Br	F = ÷ R, s = r
Madder (M. cr.)	F = almost un., s = R	O	F = — R, s = R	Y, rim R	F = R V	R Br
Cochineal (M. al.)	F = R Y	— R Y	F = R Y	Y	V R	R O
,, (M. sn.)	F = R V, s = R	÷ R	F = — R, s = R	Y	F = R, s = — R	F = — R, s = R O, D
Archil and cudbear	F = R Br, with aq. almost D s = R V, with aq = R	÷ R	F = — R s = R	Y, rim R	F = V s = V	
Alizarin S (M. cr.)	F = Br, s = — R Br	Y R	F = — Br	÷ Y	F = R V, s = V	R Br
Alizarin bordeaux B (M. cr.)	F = VR, s = V	—	F = Br, s = Br Gr	R Gr	F = V B, s = B	—
Cloth red B	F = ÷ B, s = Bl B	un.	F = ÷ V	Y, rim R V	F = R	Bl B
Ponceau 3 R (xylidine scarlet)	F = R B, s = R	un.	F = almost un., s = r	Y	F = O R, s = — R	slowly D
Palatine scarlet A	F = R Y, s = R B	—	F = ÷ R, s = r	Y, rim O	F = Br R	—
Biebrich scarlet	F = Gn, s = Gn B	un.	F = Br R	R Gr	F = — B, s = V	D in hot
Croceine scarlet 3 B	F = ÷ B, s = ÷ B	—	F = ÷ B, s = — B	Y, rim B	F = R V	D
Ponceau 6 R	F = V, s = V B	un.	F = R Y, s = r	Y	F = Br	—
Fast red E	F = R V, s = R V	÷ R	F = Br R, s = r	G. rim R Y	F = — Br R	÷ R
Azofuchsine G	F = V B, s = Bl V	un.	F = ÷ R, s = r	O Y	F = — V R, s = V Gr	D
Milling red R	F = ÷ B R, s = Br	÷ R	F = Br	R O	F = — R	—
Acid fuchsine	F = Y Br s = D, with aq. = r	almost un.	F = — R s = r	Y	F = D	almost un.

[1] ABBREVIATIONS: B = blue, Bl = black, Br = brown, D = decolorised or colourless, F = fibre, Gn = green, Gr = grey, M = mordanted, M. cr. = chrome mordanted, &c., O = orange, R = red, r = rose, s = solution, un. = unchanged, V = violet, Y = yellow, ÷ = more or dark, — = less or faint.

NAME OF COLOURING-MATTER	Conc. H_2SO_4	10 per cent. H_2SO_4	Conc. HCl	HNO_3 (sp. gr. 1·40) on F [1]	10 per cent. NaOH	$SnCl_2$ + HCl
Azocarmine (rosindulin)	F = + Gn, s = − Gn	un.	F = + R, s = R	—	F = Br	—
Fuchsine	F = − Y Br, s = Y	F = + R B, s = D	F = Y, s = − Y	Y	F = almost D	slowly D
Eosin (yellowish)	F = O to Y Br s = Y	− Y R	F = − Y R	Y	F = + R s = r	Y O
Phloxin	F = O to Y Br	slowly D	F = Y Gr	Y	F = almost un., s = r	D
Bengal red B	F = O to Y Gr	slowly D	F = D	Y	F = + R	D
Rhodamine B	F = Y, with aq. = R + Gn	+ r	F = O, with aq. = r	Y	F = r B s = D	+ r
Rosinduline 2 G	+ Gn	almost un.	Y Br	Y	almost un.	Br
Eosamin B	Bl B	almost un.	V	R Br	Br	+ r
Chromotrop 2 R	+ R	un.	− R	Y	− R Y	− R
Wool fuchsine	F = un., s = R	un.	F = un., s = r	Y	Br R	D
Acid azocarmine B	F = + B, s = Br	− V	F = R, s = R	+ Y	+ R	D
Fast chrome red B (M. cr. after dyeing)	F = Bl s = B, with aq. = V R	F = Br	F = Bl	F = Br Bl s = Br Y	F = + Br s = Br R	+ Br
Blue Dyes on Wool						
Indigo extract	F = Gn Gr, with aq. B s = Gr	un.	F = B Gr s = − B	Y, rim Gn	Y	slowly D
Sulphocyanine G	F = Gn B, s = − B	un.	F = Gn	Br	un.	D
Alkali blue 4 B	F = + R. s = R Br	un.	F = + R, s = − Gn	Gn, rim + Gn	F = Br R	—
Carmine blue	F = − Gn to Y	+ Gn	F = Gn Y to Y, s=Y	Y, rim Gn	F = Gn, s = − B	Gn, then − Y − Gn
Thiocarmine R	F = + Gn s = Gn − Gr, with aq. = B	—	+ Gn B	Gn, rim − Gn	F = + B	
Cyanole A B	D	—	F = Gn, s = D	F = D	F = Gn, s = − Gn in hot	F in hot − Y
Methyl violet 6 B	F = O, with aq. = B s = Y, with aq. = B	B − Gn	F = O s = Y	Y	F = − V s = D	B
Crystal violet	F = O, with aq. = Gn − V, s = O, with aq. = Gn	+ Gn	F = O s = Y	Y with rim + Y	F = − V	+ Gn
Alizarin astrol B	F = ÷ B, then Gn − Gr s = − r	—	F = r − B s = r − B	F = r B, then Y	—	—
Victoria blue	F = R, with aq. = B s = R	F = un. s = − Y	F = R, with aq. = B s = R	Y − Gn, rim R	F = ÷ Br s = D	+ B
Nile blue	F = R, s = Br	F = − Gn, s = − Y	F = Y − Gn, s = Y − Gn	Y − Br, rim Gn	F = ÷ R − V	—
Indazine	F = ÷ Gn − Gr	F = almost un. s = − R B	F = ÷ B, s = B	Br, rim Gn	F = − R	—
Lanacyl blue B B	Gn	almost un.	R Gn	Y Br	R	almost un.
Cyanole extra	Gn, then Y	un.	Gn, then Y	Y	Gn Gr	+ Gn
Alizarin saphirol B	Br Y	un.	Y Br	Gn	almost un.	almost un.
Alizarin irisol B	B Gn Gr	—	− B	D	F = − B, s = B in hot	in hot D
Wool blue R	Gn	almost un.	Y	Y Br	almost un.	+ B
Eriocyanine	almost un.	almost un.	Gn Y	Y R	almost un.	almost un.
Alizarin dark acid blue S N (M. cr. after dyeing)	F = V Br, with aq. = Br R	un.	F = Br s = − R	F = − Br s = V Br	F = Gr B s = − Br	almost un.
Janos blue G	Gn Y Gr	un.	÷ Gn	Gn B	un.	D
Carmine blue Ve (on silk)	Gn, then Y Br	Gn	Gn, then Y	Gn, then Y	almost un.	Gn B

Brown Dyes on Wool						
Anthracene brown (M. cr.)	F = Br R, s = Br	un.	F = Br Y, s = − Br	+ O	F = Gn Br to Bl, s = D	almost un.
Anthracene acid brown B (M. cr.)	F = R V, s = R V	un.	F = + Br, s = − R V	+ Br Y	F = − Br R, s = Br R	Gn Y
Alizarin brown G	B	almost un.	F = Bl, s = − Br R	F = Bl, s = Br R	R Br	Br, slowly D
Bismarck brown G G	F = R V, with aq. = Br s = Br R	F = + Br s = D	F = + Br s = R	—	F = + Br	− Br
Black Dyes on Cotton						
Diamine black R O or B O	F = + B, s = B	un.	F = − R, s = D	V	F = V R, s = r	D
Diamine black B O (developed with phenylenediamine)	F = + B	un.	un.	—	un.	D
Diazo brilliant black B (developed with β-naphthol)	F = + B s = B	—	F = + Gn	R V	un.	Y
Columbia black R	F = + B R s = with aq. R. V	almost un.	almost un.	+ Br	s = − R	almost D
Pluto black G	Bl—Br	un.	V	R Br	+ B	D
Vidal black	Bl Gn	un.	almost un.	s = Gr	s = Gn B	Br Gr
Sulphur black 4 B extra	F = + Bl B	F = + Bl	F = + Bl	F = + Bl, s = − Gn Y	F = + Bl	F = Br Y
Immedial black Ve extra	Gr B	almost un.	almost un.	F = − Br, s = R V Br	un.	D
Zambesi black	+ Gn	− Br	Br	V Br	− B	D
Aniline black	Bl Br	—	—	—	—	Bl Br, after washing = R Gr
Zambesi black Ve (developed with m-phenylenediamine)	F = Bl s = Gn Br, with aq. = Gr	F = un. S = − R	F = Bl s = − R	F = Bl s = Br	F = Bl	F = D
Indanthrene	F = Gn Br Gr, s = − Br	F = un.	F = un.	F = Y, s = − Y	F = − Gn B	un.
Diazo blue	B	un.	B Gr	R Br	almost un.	r
Oxamine blue R R R	+ Gn B	almost un.	+ B		V	− V
Diaminogen (developed with β-naphthol)	Bl V	un.	B	R	+ B	D
Diaminogen blue B B	V B	un.	F = + B, s = − B	R	F = V, s = − V	D
Benzo blue-black G	F = Gn, s = − B	un.	F = − Gn, s = D	= − R Br	F = + B, s = D	D
Diamine violet N	F = B Gn, s = − B Gn	+ B	F = + B, s = D	R Br	F = + R, s = D	D
Benzo azurine G G G	F = B Gn, s = B	almost un.	F = + B, s = D	Br	F = V R, s = r	D
Brilliant azurine 5 G	F = Gn B, s = − Gn	almost un.	F = almost un.	O	F = V R, s = D	D
Benzoblue B X, 2 B, 3 B (diamine blue)	F = B Gn, s = B	B R	F = V, s = D	V R, − Br	F = V R, s = D	D
Sulphur blue L extra	F = B Bl s = B, with aq. Br	F = Bl	F = Br	F = Bl s = − R Br	F = Bl	− Y
Immedial pure blue	F = + B, s = B	F = un.	F = − B, s = B	F = V R, s = V R	F = + B, s = − B	D
Yellow Dyes on Cotton						
Auramine O	F = Y Br, s = with aq. Y	− Y	F = − Y	− B	F = − Y	D
Thioflavine T	F = − R, s = D	O	F = − Y, s = Y	Br	F = un.	Br
Alizarin yellow A	Gn Y Gr	un.	− Y	Y	− Br	D
Chrysamine R	F = V R	− Y	F = Y B	—	F = r	D
Diamine yellow M	F = V R, s = V	− Y	F = V R	V	F = O R, s = − r	D
Carbazole yellow	F = + B Gn, s = B	Gn Br	F = V Br, s = D	R	F = O R, s = r	D
Chrysophenine	F = V R, s = V	almost un.	F = V, s = D	V	F = un.	D
Thiazole yellow	F = − Br, s = D	O	F = O, s = D	D	F = R Y, s = D	D
Primuline	F = Y Br, s = − Y	O	F = O, s = Y	Y	F = O	Y
Primuline (developed with resorcinol)	F = R, s = R	R	F = + R, s = R	+ R	F = + R	+ R
Fast diamine yellow A	R	un.	Y Br	Y Br	Y R	− Y
Benzo orange R.	F = B, s = B	B Gn	F = B, s = D	Br	F = R, s = Y	Br
Sulphur yellow R extra	F = − Y	—	—	+ Y	—	O Y

[1] ABBREVIATIONS: B = blue, Bl = black, Br = brown, D = decolorised or colourless, F = fibre, Gn = green, Gr = grey, M = mordanted, M. cr. = chrome mordanted, &c., O = orange, R = red, r = rose, s = solution, un. = unchanged, V = violet, Y = yellow, + = more or dark, − = less or faint.

NAME OF COLOURING-MATTER	Conc. H_2SO_4	10 per cent. H_2SO_4	Conc. HCl	HNO_3 (sp. gr. 1·40) on F	10 per cent. NaOH	$SnCl_2$ + HCl
Green Dyes on Cotton						
Italian green	+ Gn	un.	+ Gn	F = − Bl, s = R Br	− Gn Y	Y Br
Pyrogen green B	F = Bl	F = Bl	F = Bl	F = Bl	F = + Gn	F = − BrY
Sulphur green G extra	F = Bl	F = + Gn	F = + B Gr	F = + R	—	F = Gn, then Y Gr
Diamine green B	Bl B	un.	Bl B	V R	Bl Gn	D
Red Dyes on Cotton						
Turkey-red (alizarin with M. alum)	F = almost un. s = R Y, with aq. = Y	un.	F = O to − Y s = − Y	O	F = V s = V	in cold, almost un. in hot = D
Janos red B	Gn B	un.	B	R Br Gr	− V B	− R
Rhodamine 6 G	F = Y, with aq. = r s = Y, ,, = r	− r	F = Y O with aq. = r	F = O s = r	F = r Y s = − r	− r
Rhodamine S	F = Y, ,, = r s = Y, ,, = r	− r	F = Y O with aq. = r	R O	F = − r	
Fuchsine (magenta)	F = − Y Br, s = Y	F = + R B, s = D	F = Y, s = − Y	Y		− r
Safranine	F = + Gn, s = − Gn	F = R B, s = D	F = + B, s = B	R	F = almost D	slowly D, O
Induline scarlet	R Br	un.	Gn	B	almost D	
Congo red	F = + B, s = B	B	F = B, s = D	O	un.	D
Benzo purpurin 4 B	F = − B, s = B	− R Gr	F = + B, s = D	Y	F = almost un.	D
Diamine scarlet B	F = V B, s = V	almost un.	F = V, s = V	R	F = almost un.	D
Diamine red F	F = − B R, s = B	R Gr	F = V R, s = D	Br	F = O	D
Thiazine red R	R Br	almost un.	RV	+ R	Br	R V, then D
Brilliant geranine B	Gn B	− R	V	V	+ R	D
Diamine rose G D	F = R V, s = R V	un.	F = un., s = − R V	O	− V	D
Rosanthrene B (diazotised and coupled with β-naphthol)	F = Bl s = with aq. r	F = − R	F = − R	F = − R Br	− V F = − R Y	D
Erica B	F = R V, s = V	− r	F = − r, s = D	− R	F = − r B, s = D	F = + R
Geranine 2 B	F = − r Y, s = R	almost un.	F = almost un.	almost un.	F = V	slowly D
p-Nitraniline red	F = R B, with aq. = R O, s = − R, with aq. = R O	un.	F = almost un.	F = R s = R Y	R Br	D D
Brown Dyes on Cotton						
Janos brown	Bl Gr	un.	Bl Br	Br Gr	un.	Y Br, almost D
Benzo brown G	F = − Br, s = Gr	un.	F = − Br, s = − Br	− Br	F = almost un.	− Br
Benzo brown 5 R (terracotta F, alkali brown, brown for cotton R)	F = R s = R	almost un.	F = almost un. s = r	Br Y	F = almost un.	slowly D
Benzo black brown	F = Bl Gr, s with aq. = Br	almost un.	F = − V, with aq. = Br	O R	F = − Br R	almost D
Diamine brown V	F = − BR, s = Br	un.	F = almost un.	V Gr	F = almost un.	almost D
Diamine brown R	F = V, s = V	—	F = Bl	F = D, s = − R	F = R (hot), s = R (hot)	V (cold), D (hot)
Diamine bronze	B	un.	R V	R Br	− Br	D
Diazo brown R extra	Bl V	un.	s = − R	R Br Gr	almost un.	− Y
Pluto brown R	V	un.	− Br	R Br	Br R	D
Thiazine brown R	B	un.	Br	R Br	Br R	− Y
Sulphur cachou R	F = almost un.	F = − Br	F = − Br, s = − Br R	F = almost un.	F = − Br	un.
Immedial cachou O	F = Br Y	—	—	F = − Br	—	—
Sulphur brown G	F = Br Y, s = − Br Y	F = un.	F = − Br Y	F = Br Y, s = − Br	F = un.	F = − Br Y
Pyrogen brown M	F = − Br, s = Br	F = un.	F = un.	F = − Br, s = − Y	F = un.	F = un.

* ABBREVIATIONS: B = blue, Bl = black, Br = brown [illegible] M = [illegible] ... R = red [illegible] V = violet, Y = yellow [illegible]

directly on a platinum foil, give coloured vapours (*e.g.*, naphthol yellow S, picric acid, Victoria yellow).

(2*d*) If on reduction the solution is not decolorised but becomes reddish brown and in the air regains its original colour more or less, alizarin S, alizarin blue S, and the like are indicated.

(2*e*) Complete or almost complete failure of Zn + NH_3 or Zn + HCl to decolorise the solution shows thiazole yellow, mimosa, quinoline yellow S, primuline, thioflavine S, chloramine yellow, etc.

II. If the colouring-matter, in a little water and HCl, is precipitated and gives an evolution of SH_2 (detectable with lead acetate paper), and is redissolved in 10 per cent. sodium sulphide solution, the presence of a *sulphur dyestuff* is certain.

III. If the colouring-matter is insoluble in water, it is moistened and treated with a couple of drops of 5 per cent. NaOH solution :

A. If it dissolves it is reduced with zinc dust and ammonia and a paper streaked with it : (1) the rapid reappearance of the original colour in the air shows cœrulein, gallocyanine, gallein, galloflavin, alizarin blue, black, or green ; (2) the non-appearance of the colour in the air indicates alizarin derivatives, alizarin itself, nitrosonaphthol, nitrosoresorcinol, Soudan brown, etc.

B. The colouring matter does not dissolve in NaOH but is soluble in 70 per cent. alcohol : (*a*) the solution shows fluorescence, which with 33 per cent. NaOH solution either disappears (Magdala red) or does not disappear (alcohol-soluble eosin, cyanosine) ; (*b*) the solution is not fluorescent and is coloured reddish brown by 33 per cent. NaOH (alcohol-soluble induline, alcohol-soluble nigrosine, alcohol-soluble aniline blue) ; (*c*) the solution remains fluorescent (indophenol).

C. The colouring-matter dissolves in neither NaOH nor 70 per cent. alcohol [indigo alizarin black, sulphur colours (soluble in sodium sulphide)].

Green (1905) has shown that the different groups of colouring-matters may be characterised by their behaviour towards the compound of sodium hydrosulphite with formaldehyde.

RECOGNITION OF THE PRINCIPAL COLOURING-MATTERS ON DYED FIBRES. When the nature of a colouring-matter is to be studied, a dyeing test should always be made first (*see later*) and the tests described below carried out in the cold on the dry, dyed fabric, a small piece (about 1 sq. cm.) being treated in a porcelain dish with 1 to 2 c.c. of the reagent and any change observed. In testing with nitric acid, one or two drops of the latter are placed on the fabric and the colour of the drop and that of its edges noted. The hydrochloric acid solution of stannous chloride is prepared by dissolving 100 grms. of the latter in 100 grms. of the concentrated acid and 50 grms. of water. Abbreviations of the names of the colours and of the changes produced are used, and when a compound colour is formed, it is indicated by the two fundamental colours composing it ; thus combination of red (R) and yellow (Y) gives scarlet (RY), green (Gn) and brown (Br) give olive (Gr Br), etc. (*see* Note *at foot of* Table, pp. 798 *et seq.*).

To ascertain if an *indigo dye* on wool contains also *logwood* or *sandalwood*, a piece of the fabric is heated with dilute nitric acid (1 : 6) ; indigo alone gives a straw-yellow, while in presence of either of the other colouring-matters, a more or less brownish colour is obtained. Or the shredded dyed textile is heated for an hour with fused phenol on the water-bath, the phenol being decanted off, the operation repeated with fresh phenol, and the material washed two or three times with strong alcohol and pressed. If the wool were dyed with pure indigo it will be quite white, but if there were threads dyed with other colours (*e.g.*, anthracene blue, sandalwood, etc.) these are seen under the microscope to be still coloured.

According to E. Knecht (1909) the indigo on a cotton fabric may be *determined quantitatively* as follows : 4 grms. of the fabric, cut into pieces, is dissolved at 40° in 25 c.c. of 80 per cent. sulphuric acid ; the volume is then made up to 120 c.c. with water, the indigotin of the soluble sulphate being thus precipitated. This is collected on a Gooch filter, dried at 110° to 115° and weighed. It may be redissolved in a little sulphuric acid by heating on the water-bath for an hour, the indigotinsulphonic acid in the diluted solution being titrated with permanganate. The presence of basic or sulphur colours does not interfere with the estimation, since these either remain dissolved or are decomposed. If the fabric has a coating of manganese dioxide, it must first be dissolved in bisulphite.

p-Nitraniline red may be distinguished from other reds (Turkey-red, benzo purpurine, primuline, etc.) on cotton by heating the fabric at one point over a small flame ; a clear spot is formed and part of the colour sublimes on to a piece of paper placed above the fabric. The spot does not resume its original colour either on cooling or on moistening (Knecht, 1905).

TEXTILE FIBRES

Before a description is given of the processes and plant used in dyeing textile fibres, the physico-chemical properties of these may be outlined.

WOOL. Only sheep and certain goats furnish true wool used in the great textile industries. The wool fibre is readily distinguished from the hairs of other animals by its softness and fineness and by its waviness and curling, which can be seen with the naked eye. Also under the microscope a marked difference from all other hairs is easily discernible (Figs. 472 and 473). The whole filament seems to be composed of closely superposed scales, which are more or less large according to the quality of the wool. It is the saw-like or serrated structure of these scales which explains why wool readily forms a felt when rubbed, the filaments becoming more or less firmly attached one to the other.[1]

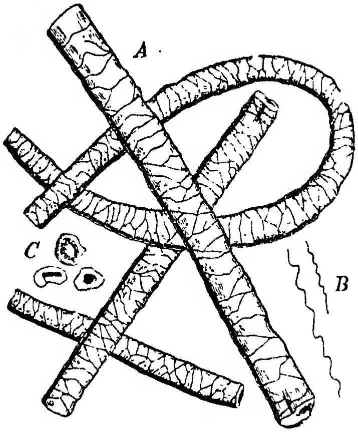


FIG. 472.

The quality of a wool is closely dependent on the breed of sheep producing it and only partially on the climate, food, and age. The yield of wool is greatest from the second to the sixth year. The finer wools, furnished generally by the *merino* breed,[2] are long, slender, soft, and very wavy, and form the so-called *combing wool* for the best woollens. Shorter wools cannot be combed but only *carded* (*Silesian*, *Saxon*), although nowadays nearly all could be combed with the improved machinery available, and a large part of the carded

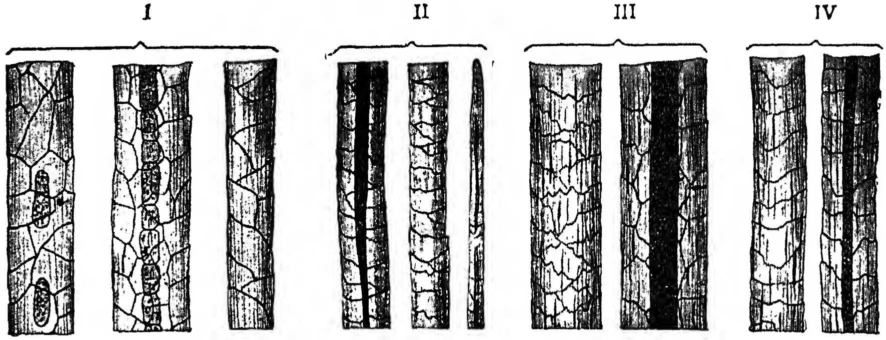


FIG. 473.

[1] The whole of the wool covering the sheep forms the *fleece*, which is kept entire even after shearing (this is done in May) owing to the scaly structure of the filaments. Wool obtained by shearing twice a year is called *bistose*, while that from slaughtered sheep is termed *skin wool* and frequently contains dead hairs, which have little affinity for colouring-matters and are often impure owing to the use of lime, arsenic, etc., as preservatives. If the sheep is washed in the tank before shearing, the wool is known as *washed*, the other being called *in grease* or *unwashed*.

The fleece (weighing 2·5 to 3 kilos) contains different parts of different qualities, and these the sorters separate by cutting. In one and the same fleece the finest wool is that of the shoulders, then comes that of the neck, stomach, flanks, and back, the poorest qualities being those of the head and legs. Certain African sheep (Morocco), and, to some extent, the Lincoln, Leicester, and Wellington breeds, give long, coarse, and only slightly curved fibres, which are used for special fabrics and for mattresses.

[2] *Merinos* are indigenous to the plains of Estremadura and Andalusia (Spain), where they were jealously guarded for some centuries, exportation being prevented. In the nineteenth century the Spaniards themselves introduced them into the Argentine, where three principal types were developed: *Rambouillet*, *Negrette*, and *Lincoln*, and a similar result followed the

wool is obtained from *shoddy*.[1] The lengths of wool fibres vary from 4 cm. to 30 cm. and the diameter from 0·014 mm. to 0·06 mm. The finer wools (merinos, Fig. 472) have as many as 13 waves per centimetre, while the more ordinary ones have only 3 (Fig. 472 *B*, natural size).

The *world's output of wool* was about 1,300,000 tons in 1903,[2] 1,450,000 in 1907, 1,530,000 in 1913, and 1,400,000 in 1920, the consumption in 1920 being 875,000 tons.

The great market for wool in Europe is at Antwerp, and the price is fixed by auction, account being taken of the yields of the various wools (Conditioning, *see later*) after washing, some of them losing 40 to 70 per cent. of their weight owing to the removal of dirt, grease, etc.; the normal or natural moisture, after washing and drying, is taken as 18·25 per cent. The price of raw wool varies somewhat from year to year and even in the same season from about 1*s.* 2*d.* to 2*s.* per kilo (pre-war). Australian wool is worth more than that from the Argentine.

Unwashed wool (Australian weighs about 160 kilos per bale), after sorting, is washed with soap and soda at 45° to 50° in vessels (*Leviathans*) provided with loose forks for mixing and, when rinsed, is dried in revolving drums by means of hot air. The washed (or salted, such as Italian or Cape wool, weighing about 110 kilos per bale) wool is then carded and

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concessions made to France and Sweden. The English introduced them, with great success, into Australia and Cape Colony. The *Electoral* breed originated in merinos which were imported in 1760 into the Electorate of Hesse, and spread into Silesia, Saxony, Würtemberg, Hanover, Moravia, and Hungary; it now furnishes a large proportion of the raw material of German and Austrian wool factories.

In England the *Cheviot* breed has assumed considerable importance and yields a long, yellowish wool, not so fine as merino. *Crossbreeds*, obtained by crossing Argentines with Cheviots, are also largely bred in England.

The *Russian breeds* are derived from pure and Saxon merinos. The commonest varieties are the *jitiugsk*, *aidarsk*, *rescetiovsk*, and *romanovsk* (this is used for furs). In France the wool of the Burgundy and of the Berry is highly valued.

Italian wools, which were once famous, are now of little importance, and only Apulia, the Tuscan marshes, and the Roman province furnish a small part of the wool consumed in Italy.

Good wool is also obtained from certain breeds of goats, such as those of *Cashmir*, which flourish in the Himalayas, nearly 5000 metres above sea-level. They furnish a very fine wool, mixed, however, with much white or grey hair; it is exported to France and Russia. The *Thibetan goat*, acclimatised also in France and in Bengal, likewise yields a valuable wool. The *Angora goat* of Asia Minor gives milk and a long wool (*mohair*) va ued for its lustre, even after dyeing.

The *vicuna* of the Peruvian, Chilian, and Mexican mountains gives a fine wool, used in certain cloths, which are now made partly from rabbit fur (the name *vicuna* or *vigogne yarn* is also applied to fabrics of wool and cotton which are quite distinct from vicuna wool). *Alpaca* is greyish, and is furnished by a kind of tall, long-necked sheep (*llama*) indigenous to Peru. *Camel-hair*, which is worked like wool, has coarse fibres, and in its natural colour is woven into certain very strong textiles, used, for instance, for the seats and curtains of railway carriages.

[1] *Shoddy* is obtained by disintegrating woollen rags (previously sorted with respect to colour and separated from those mixed with cotton) by means of an opener or *devil*, formed of a drum furnished with a number of steel points and rotating rapidly inside a second, fixed drum also provided with points; from this the rags issue in short, flocculent fibres, which are carded and then spun. This industry, started in England in 1845 and since then extended to other countries, allows of the utilisation of all woollen waste (fabrics and yarn); England alone imports from all parts of the world about 15,000 tons of woollen rags per annum. The coloured rags may often be partially decolorised by boiling them with 2 to 3 per cent. potassium dichromate and a little sulphuric acid. Admixed cotton (sewing and other) may be eliminated from the rags by so-called *carbonisation*, which consists in immersing the rags in sulphuric acid (4° to 5° Bé.), centrifuging and heating them in ovens, the temperature of which is raised to 120° to 140°. In the course of an hour the cellulose of the cotton is transformed into brittle hydrocellulose and partly carbonised, so that it can be easily removed by subsequent rubbing or by washing with water, this also carrying away the acid from the wool, which is not affected by such treatment. In some cases, hydrochloric acid vapour or aluminium chloride solution is used instead of sulphuric acid. The carbonised wool shows increased affinity for acid colouring-matters.

Also woollen fabrics which contain bits or fibres of cotton in such quantity that it is impracticable to pick them out by hand are carbonised with sulphuric acid or aluminium chloride before dyeing and are thoroughly washed after removal from the oven.

Decolorised shoddy mixed with new wool can be recognised under the microscope owing to its different colour, which often recalls the original tint.

[2] The greatest sheep-breeding countries are as follows, the numbers of thousands of sheep in 1916 being given in brackets: Spain (16,052), France (10,845), Great Britain (25,007), Italy (11,824), European and Asiatic Russia (77,000), Turkey (27,095), United States (48,483), Argentine (81,485), Uruguay (11,482), British India (23,016), Union of South Africa (35,711), Australia (69,245), and New Zealand (25,000).

combed. In some districts the washing is preceded by treatment with benzene to remove the grease (*see* pp. 486, 488).

The great European market for combed wool, not yet spun but wound into balls of 4 to 5 kilos (*tops*), is in France, at Roubaix (and also at Tourcoing and Lille), where prices are fixed at auction, although there is a considerable trade in combed wool at Bradford and to a less extent at Leipzig.

These wools are classified, according to their fineness, as A, B, . . . F, the first being the finest and the last the commoner sorts ; very fine wools are marked AA or AAA.

Before being spun the washed wool is subjected to the operation of *blending*, *i.e.*, the various qualities of wool (fine, ordinary, long, short, waste, shoddy, etc.) being mixed so as to obtain yarn of the desired count and fabric corresponding with the price and quality. To facilitate spinning and avoid felting, the wool is slightly oiled (with olive oil, commercial oleine, soap emulsion, etc., but not with non-saponifiable substances, such as mineral oils or resins, which would be difficult to remove from the fabric by washing, and would lead to irregular dyeing). In passing through the combs or cards, the various fibres are perfectly mixed and rendered parallel. The coarse strands (*tops*) are gradually converted into finer but not twisted strands, which are wound on bobbins (*prepared*) and are then, by means of ingenious, *self-acting* machines of enormous capacity, spun to the desired fineness to give, when twisted, yarn of the required count.[1] During spinning, the air of the room must be kept moistened with water vapour (*see* Vol. I., p. 337) to prevent the parallel fibres from diverging and giving a non-uniform yarn. Satisfactory weaving also requires a certain degree of moisture.

FIG. 474.

Chemical Properties of Wool. Pure wool consists of C, H, O, N, and S, the last varying somewhat in amount and being partly removed by repeated washing in boiling water. It is hence improbable that wool consists of a single chemical compound (it was at one time thought to be *keratin*, containing 4 to 5 per cent. S, but there appear to be other substances also). In 1888 Richard showed that the compounds forming wool contain NH_2 and NH groups. In a solution of alkali or a salt, wool fixes chemically

[1] The **Count of Yarn**, either cotton or wool, is given by the number of kilometres weighing 1 kilo (international count) or half a kilo (French count). In Great Britain, the count represents the number of hanks of 840 yards (1 yard = 0·914 metre) per 1 lb. (453 grms.) ; hence English count No. 1 is equal to French count No. 0·847 and to international count No. 1·694. Division of the international count by 1·66 gives the English count, multiplication of the French count by 2 gives the international count, while division of the English count by 1·18 gives the French count.

A thread spun from two yarns of count 60 has the count 30, its weight per unit length being doubled. Fine wools are spun so as to give a count of 60 to 80 or even of 120, while the commoner qualities give counts of 30 or even less.

For *silk*, the International Congress at Paris in 1900 accepted the Italian count, which expresses the weight in *denari* (1 denaro = 0·05 grm.) of a length of 450 metres, the finer yarns thus having the lower counts. Silk is often spun to a count of 12 to 20 denari, and artificial silk to 60 to 120 denari.

part of the alkali or salt. Concentrated alkali dissolves wool, forming amino-acids, the most important being *lanugic acid*, which was isolated by Knecht and Appleyard and exhibits the same behaviour towards colouring-matters as does wool.

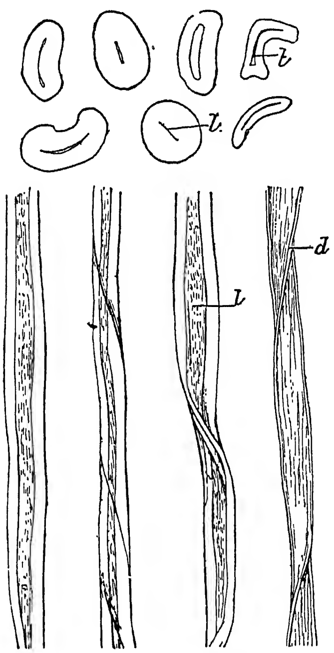

FIG. 475.
(Magnified 300 times)

It is probable, therefore, that wool contains at least one carboxyl group. The affinity of wool for acid colouring-matters (often sulphonic acids) is explained by the presence of amino-groups and that for basic dyes by the presence of the carboxyl group. Certain highly basic colouring-matters (such as methyl green) do not, however, colour wool, the acid character of which is too weak, while they colour silk, which is more markedly acid. The fixation of metallic oxides (of Cr, Fe, Cu, Al, etc.) in the mordanting of wool is due to the formation of salts with the carboxyl group.

The salt-forming property of wool can be easily demonstrated by immersing it in a hot colourless solution of rosaniline (base), which colours it red just as though it were dyed with red rosaniline hydrochloride. Knecht, Witt, and Nilsen have shown that the action of chlorine on wool is to intensify its acid character, so that it fixes basic dyes the more readily; at the same time it loses partially its capacity to felt.

Bolley found that wool decomposes potassium bitartrate in boiling solution, generating the neutral tartrate and fixing tartaric acid. In 1898 Kertesz utilised industrially, for the simultaneous production of two colours on wool, the property this shows of fixing acid colouring-matters more intensely at points where it has been carefully treated with caustic soda, the latter neutralising the carboxyl group and thus rendering the basic character more pronounced.

Wool loses much of its affinity for acid colours when treated with phosphotungstic acid, but recovers it when subjected to the action of ammonium bicarbonate (Scrida, 1909).

Of practical importance is the behaviour of wool (or cotton) waste containing ordinary oils or fats (not wool-fat), as it readily ignites owing to energetic oxidation and causes fires (*see* Pyrophoric Substances, Vol. I., p. 189).

An aqueous extract of pure wool gives a precipitate with either tannin or basic lead acetate, while true glue or gelatine yields no precipitate with the latter reagent. Pure wool contains 14 per cent. of nitrogen.

COTTON is the white down surrounding the black cotton-seed and is contained in capsules (each weighing about 30 grms., 10 grms. being cotton) which, to the number of 300 to 400, form the fruit of *Gossypium*—a shrub 2 to 4 metres in height (*see* Fig. 474). When the fruit is ripe (in America in August), the capsule opens and throws out a white tuft of cotton, which is fixed to the seeds. After harvesting, the cotton is freed from seeds by means of *cotton-gins* and compressed hydraulically into bales holding 500 lbs. (227 kilos). Cotton is produced most abundantly in North America and, to a less extent, in South America (Brazil, Peru, Colombia, etc.), and the Antilles (Haiti, Cuba, etc.). Its cultivation is also of importance in the East Indies, Syria, Macedonia, etc. Egyptian cotton (mako) is valued on account of its lustre and length of fibre. Cotton is also grown in Australia. Attempts have recently been made to cultivate it in the Italian colony of Eritrea, but without great success.

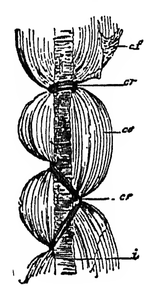

FIG. 476.
(Magnified 200 times.

The best qualities have fibres 30 to 40 mm. in length and the lower qualities (Indian) 10 to 14 mm. The fibres are 0·015 to 0·020 mm. in thickness and under the microscope have the appearance of flattened ribbons with a twist here and there (Fig. 475, the upper part of which shows the transverse sections). When treated with ammoniacal copper oxide solution, cotton swells very considerably, forming superposed capsules separated by con-

strictions (Fig. 476). By cold concentrated caustic soda solution (30° to 35° Bé.) the flat fibre is converted into a cylindrical one almost circular in section (Fig. 475 *l*; *see* Mercerisation) with a thin central channel. If immersion in the soda is prolonged for two or three minutes, during which the skein or fabric is kept stretched, and the soda is subsequently washed away while the tension is maintained, the skein will not contract and the fibres present a lustrous appearance (*mercerised cotton*) and are stronger and heavier than in their original state (soda-cellulose and then hydrocellulose are formed).[1]

[1] History and Properties of Mercerised Cotton. In 1844 J. Mercer, chemist in a Lancashire calico-printing works, having filtered a concentrated caustic soda solution through a cotton filter, noticed that the cloth had contracted somewhat and had become thicker and transparent. Before filtration the liquid had the sp. gr. 1·300, but after filtration only 1·265. On studying the phenomenon more closely, Mercer found he could reproduce it at will with yarn immersed in caustic soda solution of 20° to 30° Bé., while he established with certainty that, under such treatment, the cotton fibre shortens by 20 to 25 per cent., thickens and becomes stronger (by about 50 per cent.) and of increased affinity for colouring-matters. He showed, too, that the phenomenon is more rapid and more intense at low temperatures, while at the boiling-point no contraction occurs. Similar changes are produced by treating cotton with sulphuric acid of 50° to 55° Bé. or with zinc chloride solution.

In October, 1850, Mercer was granted an English patent (13,296) for increasing, by this treatment, the strength and compactness of cotton and its affinity for dyes.

In 1884 P. and C. Depoully patented a process for the partial mercerisation of fabrics by which parts of the fabric were brought into contact with an alkali solution; these parts contracted and caused the other parts to curl, beautiful crape effects being thus obtained.

In 1896 the textile world was astounded to see on the market samples of fine cotton of the most brilliant colours and the lustre and feel of silk. This product was prepared by the great dyeing firm Thomas and Prevost of Crefeld, according to their German Patent, No. 85,564 of March 24, 1895, which reads: ". . . . improvement in the mercerisation of vegetable fibres with alkaline or acid solutions, by subjecting the *tightly stretched* yarn or fabric to the action of alkali (caustic soda of 15° to 32° Bé.), or of acid (sulphuric acid of 49·5° to 55·5° Bé.), the stretching being maintained until washing is complete—when it is relieved spontaneously—and the shortening of the yarn or fabric thus prevented." The specification does not refer to the lustre assumed by the yarn, but this is mentioned in a later addition.

These Thomas and Prevost patents were, however, annulled a couple of years later in all countries, since various competitors found that an *identical* process had been patented (No. 4452) in England in 1890 by H. A. Lowe but had not been renewed within a year because Lowe could not find an English manufacturer disposed to make practical use of it. Large quantities of mercerised cotton are now freely produced in all countries.

The shortening of the fibre and its increased strength produced by concentrated alkali solution may be understood if the changes occurring in the fibre itself are followed under the microscope. While the fibre of ordinary cotton is seen to be a flattened empty tube with an occasional twist, that treated with caustic soda without stretching is shortened and swollen and forms an oval, almost round tube with thickened walls, but still with an internal channel; outside it shows creases and a rough surface. By mercerisation under tension, however, the fibre becomes like a straight, round tube, smooth and without visible creases outside and almost entirely filled up inside. These changes explain the silky lustre and also the increased strength, the fibre becoming more compact. Buntrock's experiments showed that mercerisation occurs very rapidly: with caustic soda of 30° Bé. the shortening of the fibre after one minute is 23 per cent. and after 33 minutes 29 per cent., which is the maximum attainable.

W. Vieweg (1908) determines the *degree of mercerisation* by a method based on the fact that, in 13 to 24 per cent. NaOH solution, cotton fixes an amount of NaOH corresponding with $(C_6H_{10}O_5)_2NaOH$, while in a 40 per cent. solution it fixes double this amount, $(C_6H_{10}O_5)_2 2NaOH$. This soda-cellulose loses its soda when washed, and the recovered cellulose has the property of taking up more or less caustic soda in a 2 per cent. NaOH solution, non-mercerised cotton fixing 1 per cent., and mercerised 1 to 3 per cent. of NaOH according to the degree of previous mercerisation. In practice this degree of mercerisation is ascertained as follows: 3 grms. of the dry mercerised cotton is shaken for an hour with 200 c.c. of exactly 2 per cent. NaOH solution in a separating funnel, 50 c.c. of the solution being then titrated with semi-normal acid and the amount of NaOH absorbed by the cotton calculated. A qualitative test for detecting mercerised cotton mixed with ordinary cotton and oxycellulose was given on p. 602. To ascertain if a fabric is mercerised H. David (1907) places a drop of concentrated soda on the fabric, which is then washed and dyed with a substantive dye; a more intense colouring on the place touched by the soda indicates that the original fabric was not mercerised.

To distinguish between mercerised and ordinary cotton, Knecht proposed the following test, which, however, sometimes gives uncertain results: A mixture of the two cottons is dyed in 5 c.c. of hot benzo purpurine 4B solution (0·1 grm. in 100 c.c. of water), about 2 c.c. of concentrated hydrochloric acid being added to the hot bath; non-mercerised cotton then becomes bluish-black, whilst mercerised remains red. If oxycellulose (formed by the action of calcium hypochlorite) is present, the cotton is dyed in Congo red and acid then added: ordinary cotton and oxycellulose turn bluish-black, whilst mercerised cotton remains red; after prolonged washing, the pure cotton then becomes red, the oxycellulose remaining black and the mercerised cotton red.

Lange (1903) soaks a piece of the fabric in saturated zinc chloride solution and then drops

The chemical characters of cotton are those of cellulose described on p. 599, purified cotton being pure cellulose. For its behaviour towards different dyes, *see* p. 772, and also later.

The world's production of cotton was about 3,500,000 tons in 1904, 5,000,000 in 1908–9, and 6,228,600 (27,703,000 bales) in 1913–14. The world's consumption was 17,500,000 bales in 1919–20, including 3,800,000 bales in the continent of Europe, 3,200,000 in Great Britain, and 6,500,000 in the United States.[1]

The conversion of cotton from flock to yarn is effected by carding or combing in a similar manner to shoddy (*see above*). Very fine counts (150) are spun in some countries, but in Italy, where at one time 30 was the finest, 60 and 90 are the usual ones, although 130 is sometimes obtained.

The immense importance of the cotton industry is shown by the following Table :—

Country	Number of Mills	Thousands of Spindles		Thousands of Looms		Thousands of Work-people	Consumption in thousands of bales of 200 to 225 kilos
	1905	1905	1914	1905	1920	1905	1905
England . .	2207	50,965	56,000	704	800	550	3640
United States, North	573	14,810	31,800	341	650	197	2168
,, ,, South	659	8051	—	174	—	120	2203
Russia . . .	227	6555	9100	155	210	350	1177
Poland . . .	56	1269	—	12	—	35	325
Germany . .	670	8832	11,400	212	190	350	1761
France . . .	420	6150	7400	206	180	90	840
Austria . . .	130	3280	4900	110	170	100	650
Hungary . .	3	104		—		—	—
Switzerland . .	68	1711	—	17	—	19	100
Italy . . .	760	2435	4600	110	150	139	560
Spain . . .	257	2615	—	68	—	—	300
Portugal . .	15	160	—	—	—	—	—
Syria . . .	35	372	—	10	—	—	80
Norway . .	9	88	—	2	—	2	12
Denmark . .	3	60	—	—	—	—	18
Holland. . .	23	376	—	20	—	17	67
Belgium . .	43	1222	—	24	—	15	100
Roumania . .	—	40	—	—	—	—	—
Turkey . . .	5	80	—	—	—	—	23
Greece . . .	—	970	—	2	—	—	15
Asia Minor . .	4	60	7400	—	—	—	18
India . . .	191	5119	1300	45	120	185	1745
China . . .	15	620	3000	2	—	—	—
Japan . . .	64	1332	—	—	40	68	900
Brazil . . .	142	450	—	23	—	20	250
Canada . . .	22	774	—	18	—	10	99
Mexico . . .	114	628	—	20	—	26	140
Total . .	6715	119,127		2120			17,511

[1] The total quantity of cottonseed produced annually throughout the world (11,000,000 tons) should yield almost 2,000,000 tons of oil, but in the United States more than one-half of the oil and cake are wasted.

on to different parts of it 10 to 12 drops of a solution containing 20 grms. of KI and 1 grm. of I in 100 c.c. of water. The fabric is manipulated and pressed for a minute and then gently squeezed between the fingers under a gentle water jet until the brownish red colour at first seen just disappears: under this treatment mercerised cotton remains deep blue, whereas non-mercerised cotton becomes white. Similar results are obtained by Hübner (1908), who immerses the

In one of the cotton mills of the United States 134 workpeople are sufficient to overlook 2000 Northrop looms, a clever workman attending as many as 20 looms, while with the less expert the number never falls below 12; these looms make 165 strokes per minute with good warp and weft.

KAPOK is a cotton-like fibre from the fruit or capsules of the tree, *Eriodendrum anfractuosum*, growing particularly in the East Indies (Java), and is separated from the oily seeds (*see* p. 499), just as with cotton. As its fibre is not very long, it is largely used for stuffing mattresses, cushions, etc. The fibre is pale yellowish-grey and lustrous, is difficult to wet and readily floats, being used also to make life-belts. From 8000 to 10,000 tons of kapok fibre is exported annually from Java, mainly to Holland.

FIG. 477.

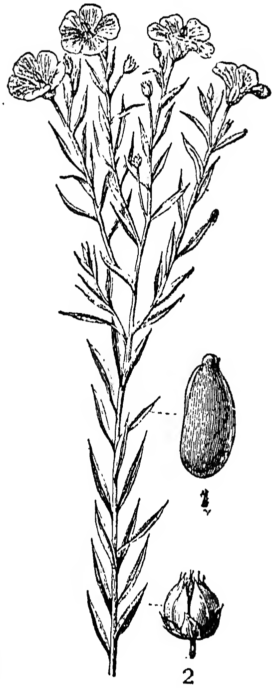

FIG. 478.

FLAX (*Linum usitatissimum*) is a herbaceous annual, growing usually in temperate regions, and reaching a height of 60 to 80 cm. (Fig. 477). It bears clusters of blue flowers which give capsules (Fig. 478, 2) containing flattened lenticular seeds (Fig. 478, 1). It was cultivated first in Egypt, then in Greece, and later in Italy and various other parts of Europe (Belgium, Holland, Russia, etc.); in Italy the cultivation has diminished very considerably, although it is still followed in some parts and is carried on in the south of Sicily for obtaining the seeds. There are two ordinary varieties which are grown for both fibre and seed: *autumn* or *winter flax*, which has a coarse fibre and is sown in October and harvested at the end of spring, the ground being left free for another crop; and that sown in March, which is pulled in the summer when the seeds begin to brown but are not quite ripe. Flax plants are pulled by hand and arranged in sheaves to dry and to mature the seeds. After removal of the latter by threshing, the plants are made into large bundles, which are left for 15 to 20 days in stagnant water, where the action of micro-organisms (*Amylobacter*, butyric bacteria) results in the dissolution of those parts of the tissues which unite the long fibres to the cortex and to the pith. The bundles are then

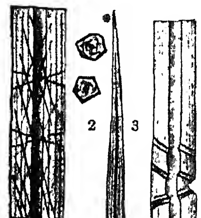

FIG. 479.
(Magnified 200 times.)

moistened and squeezed cotton for a few seconds in a solution of 20 grms. of iodine in 100 c.c. of saturated potassium iodide solution.

When cotton is mercerised with tension its strength increases by 35 per cent., and when mercerised without tension by as much as 68 per cent. The elasticity is greater in cotton mercerised without tension (27 per cent.), while with cotton mercerised under tension it is unchanged (20 per cent.). The lustre of mercerised cotton is not altered by washing or dyeing.

In order to obtain satisfactory results and a good lustre by mercerising, it is best to use long-fibred cotton; the shorter the fibre the greater must be the tension. It is also necessary to boil the cotton thoroughly and wash it completely before placing it in the caustic soda bath, as otherwise, besides obtaining less lustre, there is great danger of irregular dyeing.

The dyeing is carried out in the usual way with basic dyes, being preceded by mordanting, or, better, with substantive dyes in baths containing a little Turkey-red oil or soap, the temperature being kept low at the start to avoid non-uniformity. Old caustic soda baths, which become largely converted into sodium carbonate and so diminish in activity, can be used for soap-making.

To impart a silky feel to mercerised cotton, the latter is well washed, immersed for a few minutes in a calcium acetate bath at 0·5 Bé., pressed, introduced into a bath of Marseilles soap (1 grm. per litre), again pressed, placed in an acetic or tartaric acid bath (10 grms. per litre) and finally pressed and dried without washing.

opened and dried in the field. Instead of being *retted* in this way, flax is in some countries heated in large autoclaves for half an hour at 125° with water from a preceding operation and then for an hour with steam at a pressure of 5 atmos. The dried flax is freed from the

FIG. 480.

FIG. 481.

friable cortex by bruising between sticks, the operation being completed by blows from *scutching* knives (the waste forms the *tow*). The flax is then combed and placed on the market in large, twisted tresses of 200 to 300 grms., the price before the war being 144*s*. per quintal or 80*s*. to 96*s*. for short fibre. In Italy, a hectare of winter flax yields about 300 kilos of fibre and 900 kilos of seed, March flax giving 200 and 700 kilos respectively; in Ireland, Belgium, and Germany double as much fibre is obtained.

The number of spindles for spinning flax was, in 1912: 100,000 (flax and hemp) in Italy, 1,500,000 in the British Isles (three-fourths in Ireland), and 700,000 in France. The cultivation of flax is falling in all countries except Russia. Thus, France had at one time 120,000 hectares under flax but now has only 20,000 (in spite of Government awards of £100,000 annually to encourage its growing), about 800,000 quintals being imported (four-fifths from Russia) to supply its 700,000 spindles, 20,000 hand looms, and 22,000 power looms.

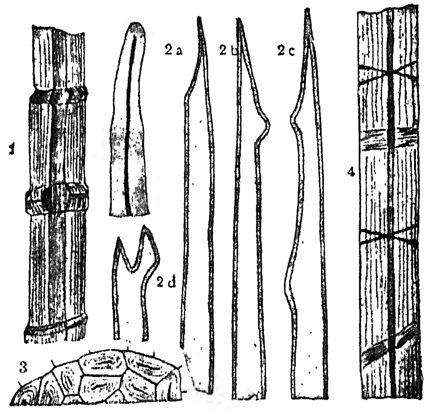

FIG. 482.
(Magnified 200 times.)

In 1913 England produced 12,000 tons of flax and imported 90,000 tons (80,000 from Russia). In 1914 Ireland had 22,860 hectares under flax and in 1918 almost 35,500 hectares, whilst the area in Yorkshire increased from 516 hectares in 1914 to 7545 in 1918.

The flax fibre has a diameter of 0·02 mm. and is readily distinguishable under the microscope from other vegetable fibres (Fig. 479: 1, spiral striation; 2, extremity of the fibre and polygonal section; 3, bruised places). The fibre is spun into yarn in the same way as with cotton, but special machines are used for the recombing and repreparing of coarse fibres, which are drawn out in the moist state to a finer thread, and, at a certain

stage, twisted. The tow from these operations is worked up by carding (*see* Shoddy). Flax can be spun by hand to a count of 300, but by machinery only to 200; certain qualities of flax can be hand-spun, for very fine work, to a count of 1400, such yarn costing (pre-war) as much as £80 per kilo.

HEMP (*Cannabis sativa*) belongs to the order Cannabineæ and bears male and female flowers on different plants (diœcious). When growing wild it branches (Fig. 480), but when cultivated for industrial purposes it grows to a height of 2 metres or more without branching and has a finer and closer tuft in the case of the female plants (Fig. 481). Of the different varieties of hemp (Manila, New Zealand, Bombay, and ordinary), the most important is the *ordinary*. It is sown very close in heavy, deeply worked soil, and is gathered in August, the plants being dried in bundles on the ground. The treatment is similar to that of flax, but with a more protracted maceration. The residue from the breaking is used to some extent in paper-making; the hemp, more or less combed, is twisted into tresses like flax and made up into bales of 150 kilos. Hemp fibres have a diameter of 0·04–0·05 mm. and are easily distinguished microscopically from other fibres (Fig. 482: 1, displaced fibres; 2, *a–d*, form of the tip of the fibre; 3, section of a bundle of fibres; 4, striation: the crossed transverse lines are not always seen, the parallel longitudinal striations being more common). The long stems are cut into three lengths of about 70 cm. and are combed first by hand and then by a machine with long, coarse points, the waste forming the first and second tow, which can be subsequently carded. A third combing is carried out with finer and closer teeth, the coarse and then the finer ribbon being passed through machines similar to but coarser than those used for cotton and wool (preparing), and finally twisted for coarse twine yarn, for canvas yarn (count of 7 to 10), etc. Two twines twisted together give a *string*, several strings combined and twisted form a *rope*, and several ropes a cable.

FIG. 483.

As well as for string, rope, etc., hemp is largely used for making coarse, strong cloth for bags, waggon covers, sails, etc. In order to render hemp fabrics more compact and durable, they are sometimes mercerised.

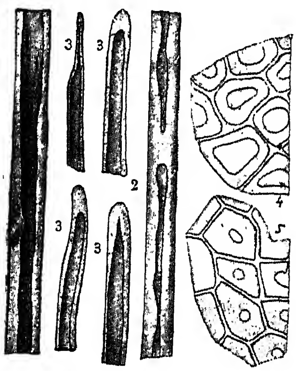

FIG. 484.
(Magnified 200 times.)

JUTE (*Corchorus capsularis* of the order Tiliaceæ) has been grown on an enormous scale in India and Bengal from time immemorial and is now replacing indigo. Even in 1851 India exported 282,350 quintals, and in 1858 the exports of jute sacks were valued at almost £240,000. These figures are now nearly doubled, owing to the development of the large works in Calcutta. In Europe its cultivation was commenced subsequently to 1830. It is grown also in South America and in the United States.

Jute requires a moist, hot climate and soil. It is sown in spring, and the plants, 15 to 20 cm. apart, mature in four months and attain a height of 3 to 4 metres. The shape of the leaves, stem, seeds, etc., is shown in Fig. 483. It is treated in a similar manner to hemp, and the bales, weighing 180 kilos, are tightly pressed for transport. The principal European centre of the jute trade and industry is at Dundee. The jute fibre is brownish yellow, and is bleached in a faintly alkaline chloride of lime bath (5° Bé.) at 25° to 30°, then rinsed, immersed in a 0·5 per cent. sulphuric acid bath for 15 minutes, and finally thoroughly washed.

Raw jute fibres are easily distinguished from other fibres under the microscope (*see* Fig. 484: 1, irregular lumen of the fibre dotted at the top; 2, fibre with broken lumen; 3, tip of fibres; 4 and 5, sections of fibre with thin or thick walls) and show more or less lustre according to their fineness.

Jute competes directly with hemp since it serves for making the same articles (sacks, packing cloth, carpets, tents, furniture coverings, etc.), but when made of jute these do not withstand washing or continuous rubbing, although they resist the action of acid or alkaline solutions rather better than cotton.

SILK. The Chinese seem to have known the *silkworm* as early as 2600 years B.C. Although they understood the preparation of silk materials, they did not at once trade with other races, but maintained great secrecy on the rearing of silkworms and strictly prohibited the exportation of the eggs.

According to tradition it was only in 150 B.C. that silkworms arrived in Japan, where they were imported secretly by the daughter of a Chinese emperor, and whence they spread later throughout the rest of Asia. They were apparently imported into Italy in the sixth century by three monks who hid them in their staves, although the manufacture of imported silk was begun in Italy three centuries earlier. From that time up to the present Italy has maintained the first place among the countries of Europe for the rearing of silkworms and the production of silk.[1]

[1] Silk is produced by one of the Lepidoptera, *Bombyx mori*, a larva which after birth when it weighs about 0·5 mgrm.), feeds on mulberry leaves (*Morus alba*) and attains the height of its development (with a weight of 3 to 5 grms.) in five weeks, passing through four moults or sleeps during which it casts its skin. It finally passes to brushwood arranged above, where it

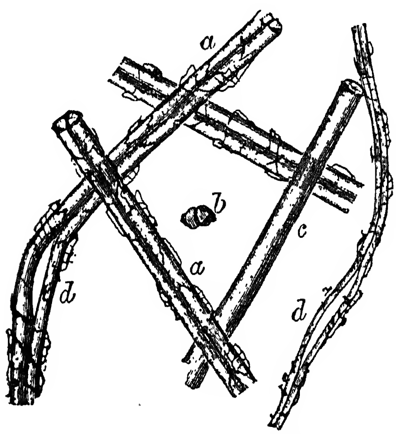

FIG. 485.—*a*, double thread (*bava*) with scales, *d*; *b*, section of double thread; *c*, isolated, smooth bava, after cleansing. (Magnified 120–180 times.)

FIG. 486.

constructs a *cocoon* with the silky exudation secreted by two long glands filled with fibroin and leading along the body beside the intestinal canal to two very fine apertures in the mouth. The two contiguous and parallel threads thus formed are immediately stuck together by a liquid (sericin) exuded by two other channels near the first pair, the result being an apparently single thread, which is either white or some shade of yellow (the double thread is shown in Fig. 485). In three days the silkworm is transformed into a chrysalis from which the butterfly originates (in 10 to 14 days) if the temperature is sufficiently high (15° to 30). The butterfly emits from its mouth an alkaline liquid with which it moistens one end of the cocoon and then perforates it and issues to proceed to the coupling necessary for the preservation of the species.

Immediately afterwards the female deposits numerous fertile eggs (*graine*), and both it and also the male die, their short life-cycle being at an end (Fig. 486). One kilo of cocoons gives 3 ounces of eggs. Part of the eggs (or of the butterflies) are selected under the microscope and are kept in a cool place until the following spring, when they are hatched by incubating for a couple of weeks in an oven, the young worms being distributed to the rearing-houses.

By means of extreme cleanliness, disinfection of the brushwood and microscopic tests of the eggs, the numerous diseases which cause havoc among silkworms at all stages (*calcino*, *flacherie*, etc.) have been partially overcome. The crossing of different varieties has also proved beneficial, and in Lombardy the use of the Chinese cross is fairly general. The silkworms from an ounce of eggs consume altogether about 12 quintals of leaves. It has been proposed to disinfect the leaves with lysoform, tachyol (ozone: Molinari, 1908), etc., but without good results.

In the twelfth century sericulture developed considerably in Sicily, and during the Middle Ages it flourished in Tuscany, Emilia, Venetia and Lombardy. In the thirteenth

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In order that a maximum yield of good silk may be obtained, the butterfly is not allowed to issue from the cocoon, since the silk cannot subsequently be readily unwound from perforated cocoons, and much waste is produced; indeed, when the cocoons are placed in water (*see later*), the perforated ones become filled with water and sink, thus breaking the thread during the unwinding. The formation of the butterfly in the cocoon is prevented by *stifling* (*i.e.*, killing) the chrysalis by heating in an oven, where the cocoon loses two-thirds of its weight. Such procedure also allows of the sale of the cocoons at the season of the year when the prices are most remunerative. Ten or 11 kilos of fresh cocoons yield 4 kilos of dry cocoons, and these give 1 kilo of silk.

An ounce of eggs yields 50 to 60 kilos of cocoons, which before the war were sold, freed from waste, at prices varying in different years from 2*s*. to 3*s*. 6*d*. per kilo; as waste are considered doubled cocoons (*doupions*), *stained* or *mouldy* cocoons, those attacked by calcino, and also incomplete, light, soft cocoons, and the flake silk or cover which surrounds the cocoons and attaches them to the brushwood.

The suffocated cocoons have an average weight which varies, more particularly with the variety, from 0·5 to 0·8 grm. The ratio between the weight of dead chrysalis and silk lies between 1·4 : 1 and 1·6 : 1 and the length of silk per gram is 900 to 1500 metres; the thread (bava) varies in thickness from 0·018 to 0·030 mm.

The *cocoons* are first placed, a few at a time, in basins of almost boiling water and are rubbed with a hand-brush of twigs, to which the tangled filaments covering the cocoons become attached. Among these filaments is that by which the cocoon can be completely unwound. The other filaments form the floss, which is worked up with the other waste (*see above*). Five (or more) of the threads are attached to a *reel*, which revolves rapidly and completely unwinds the cocoons. The latter float in hot water, which softens and dissolves part of the gum uniting the threads, while the remainder of the gum dries again on the reeled silk, joining the five threads to a single filament constituting raw silk. As one cocoon is finished, it is replaced immediately by another so as to form a homogeneous thread. The chrysalides remaining form about 70 per cent. of the weight of the fresh cocoons and contain 22 to 26 per cent. of oil (fetid); they are generally defatted and sold as nitrogenous fertiliser (for hemp, etc.) at 13*s*. or 14*s*. per quintal. Cocoons which do not unwind regularly also pass into the waste.

Good cocoons give as much as 800 metres of good silk and the count of the single thread varies from 1·5 to 4 denari according to the breed of silkworm; the tenacity lies between 5 and 12 grms. and the elasticity between 80 and 150 mm.

White or greenish yellow cocoons give white or almost white (Chinese) silk and the yellow ones golden-yellow silk. The following types of silk are distinguished commercially: European, Japanese, Chinese, Canton, Bengal, *tussah* (Chinese wild silk), and Indian tussah, and of each of these there are various qualities.

In the raw silk trade the variations of the count are indicated; thus, first-quality silk from 8 to 10 denari is marked $\frac{8}{10}$, first-grade tussah of 40 to 45 denari, $\frac{40}{45}$, etc.). The price of tussah silk (16*s*. to 24*s*. per kilo) is less than half that of fine European silk, but the prices vary from year to year.

With Asiatic silk it is always stated whether spun in Europe or on the spot; the latter gives much more waste in the subsequent operations.

Raw silk threads are seldom made into textiles (then called raw silk) and real silk thread is obtained by joining two or more threads of raw silk and twisting them to form the *tram silk* or *organsine* (warp) used in weaving.

To this end the raw silk is first wound on bobbins, from which it passes through felted forks—to free it from down—to other bobbins. It is then ready for twisting, which is carried out in different ways for *tram* silk and for *warp* (organsine). For the latter the best silks are used, these being at once twisted from right to left, the product being known under different names according as the number of the twists per metre are 244 to 440, 440 to 488, or 488 to 610. The twisted threads are then joined in twos, threes, or fours, the combined threads being twisted from left to right (or *vice versa*)—380 to 450 twists per metre for taffeta, 320 to 360 for satin, 550 to 560 for velvet, and 2200 to 3000 for Chinese crape. Before dyeing or bleaching, the raw organsine is *ungummed* or *stripped* for about 30 minutes in boiling neutral soap solution (25 to 30 per cent. of soap calculated on the silk). In order to remove the gum and to obtain a maximum lustre, a second boiling soap bath is used, and finally a third. The *boiled silk* weighs about 25 per cent. less than the original organsine. When the organsine is to be dyed a pale or delicate colour, it is subjected to special treatment with sulphur or hydrogen peroxide (*see* Vol. I., pp. 267, 278); tussah organsine (brownish) is only bleached with hydrogen peroxide.

In preparing *tram silk* the raw threads are not immediately twisted, but are first joined in fives or tens (or more) and then twisted, but only with 80 to 125 twists per metre. The cleansing with soap is carried out at 35° and the colouring-matter is readily destroyed by immersion for 15 minutes in an aqua regia bath (2·5° to 3° Bé.) at 20° to 25°, and thorough washing with water. The white tram (so-called *souple*) has lost in these operations only 5 per cent. of its weight; if it is to be dyed a pale tint it is then sulphured. When a more lustrous tram is required for obtaining special effects in textile design, it is subjected to *boiling* like the organsine.

Silk Waste, including *doupions* (cocoons formed by two larvæ in the same covering; these cannot be unwound in the ordinary way), pierced cocoons, the waste from twisting (2·5 per cent. in Italian and 8 per cent. in Asiatic silks), stained (mouldy) cocoons, diseased cocoons, small or incomplete cocoons (from inert worms), silk tow, etc., constitutes 25 to 35 per cent. of the total

century it was started in France, being introduced by Italian immigrants. The Arabs introduced it into Spain in the year 740.

In 1443 Florence contained 84 large silk factories and in 1580 Milan began to acquire the ascendancy, but fell back later, to advance again in the middle of the nineteenth century. In 1804 Como had only 920 looms, which increased to 1800 in 1858, while Lyons possessed 10,000 looms as early as 1685, 40,000 in 1834, and 65,000 in 1852 (present conditions are indicated later).

Raw silk consists of 60 to 70 per cent. of **Fibroin** (the fundamental constituent of pure silk) and 25 to 35 per cent. of **Sericin**, which is the gum surrounding the threads and holding them together, and can be easily eliminated with hot water and soap or, partially, with hot water alone.

Various formulæ have been attributed to fibroin: $C_{15}H_{20}O_6N_5$ (Schützenberger), $C_{71}H_{107}O_{25}N_{24}$ (Bourgeois, 1875). From the chemico-tintorial point of view, silk has the character of an amino-acid (or of the corresponding internal anhydride), but its acid nature is more marked than that of wool. The decomposition of fibroin by means of hydrochloric acid gives glycocoll, aminopropionic acid, tyrosine, *l*-leucine, and other amino-acids (E. Fischer).

The formula $C_{18}H_{15}O_8N_5$ is ascribed to **Sericin**, which closely resembles fibroin, but gives large proportions of diamino-acids. It is thought by some that the silkworm contains only fibroin, and that at the moment when the thread is produced this is transformed superficially into sericin under the influence of air and moisture. The yellow colour of certain raw silk is due to a natural colouring-matter, **Carotin** (Dubois' hydrocarbon).

Under the microscope raw silk has the appearance of slightly flattened, cylindrical, transparent threads, not very smooth on the surface, and composed of two bave joined by the sericin (which can be distinguished from the inner part or fibroin) and thinly covered with an adhesive soluble in hot water and different from sericin, which dissolves only in hot soap solution.

In many cases the **Dyeing** of silk, especially with mordant dyestuffs, is similar to that of wool. Under all circumstances, however, the silk should be thoroughly cleaned before dyeing, and as in spinning and weaving the silk is treated with dressing (soap emulsion, vaseline oil emulsion, soluble starch, etc.) to facilitate the operations and sometimes also to increase the weight, both yarns and fabrics (even if white) are subjected to rapid cleansing with hot soap solution (80° to 85°) containing a little sodium carbonate, and are then well rinsed in tepid water.[1] If the wares are to remain white, they are sulphured (*see* Note) or treated with hydrogen peroxide solution, the characteristic rustle (*scroop* or *crackle*) of silk being imparted by immersion in a 1 to 2 per cent. sulphuric or acetic acid bath, centrifugation and drying without rinsing.

Dyeing is in general carried out in soap baths, using one-third or one-fourth of the soap solution remaining after the boiling of the raw silk, acidifying it with sulphuric acid

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crop of cocoons and often goes under the name of floss (sold before the war at 4*s*. to 6*s*. per kilo; real floss cost 6*s*. to 7*s*. per kilo). It is worked very similarly to cotton and to woollen rags by means of special carding and combing machines, giving first a kind of wadding and then ribbons and threads with parallel fibres. These can be converted into yarn called *chappe*, which is consumed in large quantities as it costs less than one-half as much as pure silk and for some fabrics (velvets) is a good substitute for ordinary silk. The waste from the carding and combing of chappe is also spun, giving *bourettes*. In Italy a large company with seven works enjoys a kind of monopoly in this trade; they work up foreign waste and part of the native waste, the Italian Government imposing a small export duty which acts detrimentally against the spinner and forms a protective duty on foreign waste yarn.

[1] It is generally necessary to ascertain, before dyeing, what will be the loss in weight of the silk during ungumming or stripping. White Italian silk loses on an average 21·5 per cent.; Japanese, 20 per cent.; Canton and Chinese, 24 per cent.; raw yellow Italian, 24 per cent.; and chappe, 4 per cent. The loss, which includes also any weighting of the yarn with vaseline, soap, oils, glycerine, etc., is determined as follows: 50 grms. of the silk is manipulated in a solution of 15 grms. of seasoned Marseilles soap of good quality in a litre of hot water, which is allowed to boil gently for half an hour, and is then removed, pressed or centrifuged, boiled for a further period of 30 minutes in a soap bath similar to the first, and washed thoroughly with water until the latter remains clear; after being centrifuged, the silk is dried in an oven until of constant weight. The loss of weight on stripping is referred to 100 grms. of dry silk, so that allowance should be made for the *normal humidity* (11 per cent.) of silk.

boiling and agitating. The silk is immersed in this emulsion for a time and then removed, the bath being diluted with water and the colouring-matter (acid or basic); the dyeing is begun at 35° to 40°, the temperature being gradually raised almost to the boiling-point. Acid colouring-matters are fixed by silk also from a hot acidified aqueous solution, but the tints are not so lasting.

The dyed silk is rinsed in water and transferred to the acid bath to obtain the *crackle* which becomes more pronounced as the acidity and temperature of the bath are raised, but the acid remaining in the dry fibre slowly attacks it, with injury to its tenacity and elasticity.

Nowadays silk is usually *weighted*, *i.e.*, impregnated with various substances (organic and inorganic), in order to increase its weight (by 30 to 40 per cent. and sometimes, with black silk, even by 300 per cent. or more). Silk possesses, indeed, the property of absorbing from solution large quantities of tannin; this can be fixed by means of salts, and fresh tannin can then be absorbed, and so on. Successive amounts of insoluble metallic salts (tin salts, phosphates, silicates, etc.) may also be precipitated on silk. To weight white silk, the boiled silk is soaked for an hour in a stannic chloride bath of 25° to 30° Bé. (at one time pink salt, $SnCl_4,2NH_4Cl$ (*see* Vol. I., p. 781) was largely used, but at the present time, crystallised tin salt, $SnCl_4,5H_2O$, is mostly employed), manipulated for 30 to 40 minutes in a hot disodium phosphate bath (4° to 5° Bé.) washed slightly with water, introduced into a sodium silicate bath (3° to 4° Bé.) and again washed. Treatment with this series of baths (stannic chloride, phosphate, and silicate) is repeated several times, according to the degree of weighting desired; five such repetitions give a weighting of 100 to 120 per cent. (the weight being doubled).[1] Weighted silk can be dyed, and in the pre-

[1] The phenomenon of *weighting* is explained, according to Sisley (1911), by regarding silk as a *colloid* (*see* Vol. I., p. 106), which absorbs hydrogels (*e.g.*, stannic) of various salts of polybasic acids, but many substances which give precipitates and insoluble salts do not serve for weighting, since they are not firmly retained by the silk fibre—and are therefore eliminated during washing and dyeing—and are not dyed. The weightings which have given the best results in practice are: (1) tin hydroxide (used as early as 1869 in a Lyons dyeworks); (2) tin phosphate; (3) tin silicophosphate; (4) tin and aluminium silicophosphates. Sisley (1896) showed, and Fränckel and Fasal (1897) and Severini (1906) confirmed, that weighting is due purely to a physical and not to a chemical phenomenon, since the weighting bath undergoes no chemical change and no alteration in concentration. Further, when silk soaked in stannic chloride is washed with water, the precipitated stannic hydroxide which is formed in abundance as a result of hydrolysis is not fixed by the silk and is derived from the chloride on the surface of the thread, that *absorbed* inside the fibre remaining as a kind of colloidal solution of stannic hydroxide in hydrochloric acid; the acid diffuses into the fibre, which retains it, whilst the stannic hydroxide is fixed as a gel and does not influence the feel and lustre of the silk. The absorption of stannic chloride is avoided if the silk is previously treated with tannin. In 12 hours silk which has absorbed 11 per cent. of tannin fixes from a stannic chloride bath of 30° Bé., only 1·25 per cent. of SnO_2, while silk without tannin fixes about 12 per cent. of SnO_2 from the same bath; these different silks also take up varying quantities of colouring-matters. When washed, the stannic hydroxide formed on the fibre is $Sn(OH)_4$ or $SnO_2,2H_2O$, retaining small amounts of HCl; the washed silk is therefore introduced into a bath of sodium carbonate, which forms a labile compound of Na_2CO_3 and $SnO_2,2H_2O$, this being decomposed by acid with formation of a tin hydroxide insoluble in acid and in subsequent stannic chloride baths.

Boiling or treatment with a soap bath of washed silk containing $SnO_2,2H_2O$ results in the separation, in a firmly fixed condition, of the hydrate Sn_4O_2,H_2O, *i.e.*, $Sn_4O(OH)_2$, which has, however, but little affinity for phosphates and silicates (Gianoli, 1907). Weighting with stannic chloride gives a regular increase of 10 to 12 per cent. in the weight for each separate operation on the same silk. In weighting with tin phosphate (after the chloride bath, the silk is passed into a hot disodium phosphate bath and then washed thoroughly with water, the operation being repeated if necessary), the first operation gives an increase of about 20 per cent., but subsequent operations produce larger increases; the third may give as much as 35 per cent. Silk alone has no affinity for salts of polybasic acids (phosphoric, tungstic, etc.), but if it is first passed into a tin salt bath it fixes them, for example, as SnO_2,Na_2WO_4 or SnO_2,Na_2HPO_4 (sodium phosphostannate, insoluble in water but soluble in concentrated sodium phosphate solution); only phosphates containing hydroxyl groups are fixed by tin, so that trisodium phosphate and sodium pyrophosphate are not fixed. If the sodium carbonate bath follows the chloride bath, less sodium phosphate is subsequently fixed. Treatment of the silk in the acid bath results in the removal of the whole or a good part of the sodium. When the silk has been treated in the first sodium phosphostannate bath, it is washed and introduced a second time into the stannic chloride bath, the double decomposition thus produced resulting in the formation of insoluble phosphate of tin, which is fixed on the fibre, and of sodium chloride, which passes into the bath while at the same time the silk becomes impregnated anew with $SnCl_4$—this fixing tin hydroxide on the fibre when the latter is washed. This tin hydroxide gives fresh sodium phosphostannate when introduced into a second disodium phosphate bath, while the bath, which becomes impoverished in soda, continually increases in acidity and the weighting of the silk increases during successive operations.

Still higher weighting is obtained if the sodium phosphostannate silk is introduced into one

paration of black silk, the weighting may be increased considerably by passing the weighted white silk (washed with a little soda) into a cold bath of ferrugine (a slightly acid solution of basic ferric sulphate prepared by heating a solution of ferrous sulphate with sulphuric and nitric acids), slightly washing the silk thus coated with oxide of iron and immersing it in a bath of potassium ferrocyanide (acidified with HCl) which colours it blue. It is then placed in an almost boiling tannin bath (*e.g.*, chestnut extract), next in a tin bath to fix the tannin, and finally in a hot bath of logwood extract to obtain an intense *black tint;* the dyed silk is rinsed in soap solution or an acidified oily emulsion, livened in a sulphuric acid bath, centrifuged and dried. By repeating the tannin and metallic baths ten or fifteen times, weighting of 300 to 400 per cent. may be obtained. Black silk weighted to the extent of 400 per cent. and partly attacked shows under the microscope a heavy incrustation round the fibre (Fig. 487); much of its strength has been destroyed, and under the action of sunlight it undergoes rapid corrosion (umbrellas of heavily weighted black silk split even without using). O. Meister at Zurich (1902) and independently G. Gianoli at Milan (1904; Ger. Pat. 163,622) found that this inconvenience can be largely avoided by means of a thiocyanate bath. In 1906 the Società della stagionatura della seta di Milano (as a result of investigations of Sisley at Lyons and of Gianoli and Colombo) filed a patent in America for the preservation of weighted silk by introducing it in a bath of thiourea faintly acidified with citric acid; U.S. Pat. 873,902, was granted in February, 1908, and appears to give excellent results in practice.[1] O. Meister (1910) suggests the use of formalde-

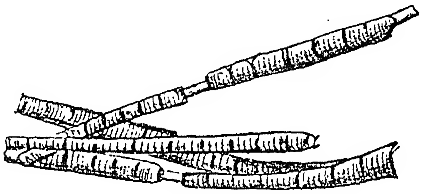

FIG. 487.

or several more or less concentrated and more or less hot sodium silicate baths. By this means part of the phosphate residue united to the tin oxide is replaced by silica, the compound $3SiO_2,Na_2O,SnO_2$, being formed; the silicate bath becomes acid and contains trisodium phosphate. In the acid bath, this silk readily loses sodium, being formed of insoluble tin trisilicate. This weighting was patented by Neuhaus in 1893, but had been previously used in France.

The highest weighting of silk is obtained by following repeated phosphate baths with a bath of an alum salt, as was proposed by Puller (Crefeld) (Fr. Pat. 254,659 of 1906). In this way the aluminium is fixed as phosphate and a little sodium passes into solution. After washing this silk is passed into a sodium silicate bath and has the property of fixing much more silica than in the case described by Neuhaus; further, the silk loses practically nothing in the acid bath, since the sodium of the tin silicophosphate has been replaced by aluminium. Nicolle and Sisley (1911) found that various other salts may be used in place of those of aluminium, but that only those of zinc gave good results in practice.

This general theory of Sisley on the phenomenon of weighting of silk is not universally accepted. P. Heermann (1904–1911) holds that while the silk is immersed in the stannic chloride bath the latter diminishes in concentration, and part of the tin remains fixed even when the silk is washed with water; he also regards the formulæ of the salts fixed on the silk as different from those given by Sisley.

[1] In *determining the weighting of silk* 2 grms. is boiled for two hours in a soap bath (30 grms. soap per litre) and then for at least an hour (to expel the ammonia) in a sodium carbonate bath at 1·5° Bé., the water evaporated being gradually replaced. It is then rinsed well with water and dried and the nitrogen in 0·6 to 0·8 grm. determined (as was suggested by St. Claire Deville in 1878) by Kjeldahl's method (*see* p. 11); from this the quantity of true fibroin can be determined, knowing that 5·455 parts of fibroin correspond with 1 part of nitrogen. With black silk containing cyanide (Prussian blue), the latter must be previously eliminated. In order that the fibroin may be acted on as little as possible, P. Sisley (1907) separates it as follows: 2 grms. of the fabric is boiled for 10 minutes in 25 per cent. acetic acid, washed, heated for 10 minutes at 50° in a 3 per cent. sodium phosphate ($Na_3PO_4,12H_2O$) solution, washed again, and boiled for 20 minutes in a bath containing 3 per cent. of soap and 0·2 per cent. of soda; this procedure is repeated, the tissue being washed and dried and its nitrogen-content determined. The percentage weighting p (the increase in weight of the original silk) is given by $p = 100(g - c)/c$, where g indicates the weight of the dyed silk while c represents that of the raw silk (*i.e.*, fibroin + sericin + 11 per cent. moisture) or fibroin + normal loss on stripping (21·5 or 24 per cent.; *see* preceding Note). A silk is said to be weighted 50 per cent. when 1000 grms. of raw silk give 1500 grms. of dyed silk.

During recent years, another simple method has been used for determining the ordinary tin silicophosphate weighting: 2 grms. of weighted silk of known moisture content (*e.g.*, 10 per cent.) is treated for an hour in a platinum dish with 100 c.c. of a cold aqueous 2 per cent. hydrofluoric acid solution; the latter is poured away and another 100 c.c. of the acid added and left in contact with the silk for an hour. The silk is washed seven times with successive amounts of 150 c.c. of water, pressed, and dried at 100° to 105° until of constant weight. If the latter is 0·95, then 2 grms. of moist silk = 1·8 grm. dry silk, and 1·8 − 0·95 = 0·85 (weighting).

hyde bisulphite (1 to 5 per cent. bath) to check this corrosion, while Berg and Janhoff (1911) prefer the use of hydoxylamine. The use of a *diastofor* bath (*see* p. 140) after dyeing has also been proposed. Silk weighted with $ZnCl_2$ is preserved in a thiosulphate bath (Herzig, 1908).

STATISTICS. The world's production of *raw silk* (excluding the local consumption of the Far East, this being valued at about 55,000 quintals for China and 47,000 for Japan, in 1906, and about one-third more in 1907) is shown in quintals by the following Table (the pre-war value of raw Italian silk may be taken as 32*s*. to 36*s*. per kilo):

Locality.	Average for the years					
	1886–1890	1896–1900	1901–1905	1906	1909	1913
Italy	33,110	42,150	43,260	47,450	42,500	35,400
France	6,920	6,500	5,910	6,050	6,740	3,500
Spain	720	830	800	560	800	820
Austria-Hungary	2,650	2,720	3,150	3,420	3,800	2,600
Anatolia (Brusa)	1,860	4,020	5,180	5,540		
Syria and Cyprus	3,030	4,560	4,870	4,700	15,700	11,300
Salonica, Adrianople	1,340	1,620	2,350	2,570		
Balkan States	—	470	1,410	1,850	3,150	1,250
Greece and Crete	21	410	640	750	700	2,100
Caucasia	—	2,760	3,910	4,550	5,400	3,850
Turkestan	94	1,680	4,680	6,280		2,250
China, exported from Shanghai	27,570	45,080	42,270	42,620		58,000
China, exported from Canton	1,277	20,210	21,280	19,620	157,200	27,800
Japan, exported from Yokohama[1]	20,560	34,590	48,650	59,920		118,500
India, exported from Calcutta and Bombay	4,360	2,930	2,560	325		1,000
World's totals, quintals	116,000	170,530	190,920	209,130	242,000	270,000

In China the exportation of real silk tends to diminish, but that of *wild silk* (or *tussah*) increases; this is produced by *Anterea mylitta* and is readily recognised under the microscope (Fig. 488). China exported 1,260,000 kilos in 1900; 1,325,000 in 1903, and 2,000,000 in 1904.

To the quantity of raw silk produced in Italy from home-grown cocoons must be added that obtained from cocoons imported from abroad, viz., 3000 quintals in 1893; 7320 in 1898; 11,000 in 1903, and 13,000 in 1906. The mean annual importation from 1901 to 1905 of cocoons (calculated dry) was 37,736 quintals (46,000 in 1906) with a mean yield of

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Hence, if the raw silk is calculated to lose 24 per cent. on stripping, the weighting will be $0{\cdot}95 : 0{\cdot}85 = 76 : x$ (76 is the percentage of silk remaining after stripping) and $x = 68$; hence the dyed dry silk contains 76 parts of dry stripped silk (or 100 of raw silk) and 68 of weighting, total 144. The silk was hence weighted 44 per cent. Gianoli and Colombo (1907) showed, however, that in some cases when metastannic acid is formed on the fibre, *e.g.*, by the fixation of tin salts with sodium carbonate, the whole of the weighting is not eliminated by hydrofluoric acid, even when this is followed by a bath of HCl. A more certain result is then obtained by the old method (*see above*) or by using first soda and then potassium hydrogen oxalate. P. Heermann (1909) proposes to modify the alternate treatment with hydrochloric acid and caustic potash (Ristenpart, 1908) of black on tin salt and catechu, by replacing the caustic potash with a solution of normal caustic potash and concentrated glycerine (28° Bé.) in equal parts, the latter preserving the silk, readily dissolving Prussian blue (by treatment for an hour in the cold or 10 minutes at 80°), but leaving the oxide and tannate of iron unchanged.

[1] In Japan a second crop of cocoons (bivoltine) is gathered in summer, and a third (trivoltine) in autumn. About 60 per cent. of the total crop is obtained in the spring, 12 per cent. in the summer, and 28 per cent. in the autumn.

Japan also produces a considerable amount of green wild silk—of *Bombyx yamamai*, which feeds on chestnut and oak leaves (the wild silkworm of India eats castor oil leaves).

1 kilo of silk per 4 kilos of dry cocoons (at 7*s.* to 9*s.* 6*d.* per kilo) or per 11·5 kilos of fresh cocoons.

To the 50,000 quintals of raw silk yarn produced in Italy must be added 24,000 quintals of silk simply treated and imported from the Far East to be spun and twisted, but only about 10,000 quintals are woven in Italy, the rest being exported (50,000 quintals, besides 39,000 of twisted).

The Italian weaving industry is capable of considerable extension, its produce being valued at only £3,200,000, while Switzerland[1] (with 35,000 looms) produces silk fabrics to the value of £5,600,000, France[2] (with 140,000 looms) £19,600,000; England about £13,600,000 (importing £8,800,000) with 87,000 looms, and about the same for Germany. If Italy were to weave the £8,000,000 worth of yarn which it exports, the value would be increased to £16,000,000 (a kilo of fabric costs about double as much as a kilo of yarn) while 200,000 more workpeople would be employed.

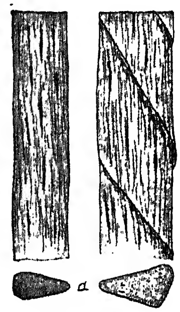

FIG. 488.

The Italian silk industry has passed through various crises, not on account of excessive production—since working on stock is not usual with silk articles and the demand is often greater than the supply—but owing to various circumstances, not the least among which are the tariffs raised against Italy as retaliation for the protection of many Italian industries by the tariff of July, 1887. The most acute crises of the Italian silk industry were those of 1893 and 1903, which were the cause of numerous financial disasters, and that of 1907–1908, the effects of which are still felt, and which resulted from the great American crisis and is now being aggravated by French and Japanese competition. The quinquennial average price of raw Italian silk fell gradually from 62·1*s.* per kilo in 1876–1880 to 38·1*s.* in 1901–1905, mainly owing to increase in the world's production (*see* Table, p. 818). In 1906 and 1907 a rise in price of raw silk occurred; thus, that of organsine sublime (count $\frac{18}{20}$) was 40*s.* per kilo at the end of 1905, and rose to 49*s.* 6*d.* towards the end of 1906 and to 60*s.* 6*d.* in August, 1907, after which a fall took place owing to the American crisis.

Silk-twisting in Italy in 1910 employed 800,000 spindles (four-fifths in Lombardy and the remainder in Piedmont), which produced 4,500,000 kilos of organsine and tram, about one-half from imported raw silk.

[1] Switzerland has two very important centres at Zurich and Basle, where the output of silk goods is continually increasing, although the production of cocoons is gradually diminishing In the canton of Ticino, where the silkworm is reared, the cocoons produced have diminished from 187,500 kilos in 1872 to 58,000 in 1904, while there has been a corresponding increase in the importation of raw silk from China, Japan, and Italy. The importation rose from 514,400 kilos in 1893 to 637,000 (worth £960,000) in 1902, but about one-third of this, after being twisted in the Swiss factories, is exported to Germany, Russia, and Italy. In the canton of Zurich alone in 1900 there were at work about 21,000 hand-looms and 13,330 power-looms for silk and mixed silk fabrics.

The Swiss exports of pure silk tissues in 1893 were 966,700 kilos (£2,506,100), those of mixed tissues being valued at £580,000. In 1903 the exports of silk fabrics were 1,760,300 kilos, worth £3,780,000, while the total imports in the same year were 149,000 kilos (£330,800) of silk fabrics and also mixed fabrics to the value of £112,000. One-half of the exports goes to England. The silk ribbon and embroidery industry of Switzerland is steadily advancing.

Germany is a large importer of raw silk (about 3,000,000 kilos, largely Italian), and, besides supplying home demands, exports considerable quantities of manufactured goods (*see* Table *later*).

Russia consumes about 1,500,000 kilos of raw silk annually.

[2] None the less interesting is the condition of affairs in France, although the production of fresh cocoons is only 8,000,000 kilos (1905). The imports of raw silk are calculated to be about 9,000,000 kilos, and the silk industry (almost entirely concentrated in the city of Lyons) occupies one of the foremost positions among French industries. The province of Lyons contains more than 25,000 power-looms for silk-weaving, in addition to a larger number of hand-looms. In order to reduce the importation of raw silk and increase that of cocoons, and so encourage the direct spinning of the latter, the French Government in 1892 offered a premium of £16 for every new four-threaded basin established, but the results did not come up to expectations.

While in 1893 the production of silk goods was valued at £15,150,000, in 1902 it reached £17,800,000. The French exportation of silk wares of all kinds amounted in 1896 to 4,220,000 kilos, worth about £10,000,000, while in 1904 it rose to 5,700,000 kilos, of the value of £13,200,000 (including about £1,200,000 worth despatched by parcel post).

The value of the products woven in Lyons in 1904 was £16,360,000, in 1905 £15,640,000, and in 1906 £17,040,000. In the department of Saint-Etienne the output of silk *ribbon* in 1906 was valued at £3,760,000, one-third of it for export.

The French home consumption of silk wares is about 4,000,000 kilos, this large amount helping considerably to maintain the silk industry in an active condition.

The *silk-waste* which was produced in Italy in 1910 (and was exported to the extent of two-fifths while the remainder was worked up in Italy) amounted altogether to 5,300,000 kilos of the value of £500,000.

Silk, carded and combed in Italy, amounts to about 1,500,000 kilos and the chappe yarn to almost 900,000 kilos, of which 200,000 kilos are consumed in Italy and the rest exported. Six thousand workpeople are employed in the treatment of waste, the ten establishments in this trade containing about 80,000 spindles in 1912.

During the past twenty-five years the silk weaving industry has become of considerable importance in the United States, where raw silk is almost free from customs duty, while the manufactured products (yarn and fabric) are very heavily taxed. These conditions have led to the rapid development of American spinning and weaving.[1] The importation of raw silk into the United States shows continuous and rapid increase, the annual averages being: 1881–1885, 15,300 quintals; 1886–1890, 23,100; 1891–1895, 31,300; 1896–1900, 43,500; 1901–1905, 65,300 quintals, which is about one-third of the world's production (excluding the local consumption of the Far East).

The countries with large outputs of cocoons are not always large consumers of silk wares, while in general large consumers are not producers. Italy has a total internal consumption of 6500 to 7500 quintals of silk articles, and the relation between home consumption and exportation for the principal countries in 1899 was as follows:

	Home consumption. Per cent.	Exports Per cent.		Home consumption. Per cent.	Exports Per cent.
France	61	39	Switzerland	5	95
Germany	60	40	United States	95–100	0–5
Austria	88·5	12·5	China	about 50	about 50
Italy	20	80	Japan	,, 50	,, 50

As regards the quantity of raw silk passing through their conditioning establishments, the two principal silk markets in the world are Lyons and Milan, which together receive about two-thirds of all the silk conditioned in Europe, the separate amounts being as follow:

	Milan	Lyons
1881	36,652	53,480
1890	43,477	44,072
1900	72,335	60,418
1903	83,725	66,508
1905	94,391	70,102
1906	101,484	71,719
1908	95,293	73,728

In 1908 13,186 quintals arrived at Lyons from Europe, 7564 from the Levant, and 50,000 from the Far East; and at Milan, 67,187 quintals from Europe, 1477 from the Levant, and 36,530 from the Far East. During recent years Milan has lost ground compared with Lyons.

SEA SILK (*Byssus*) is found in tufts protruding from the shells of a mollusc (*Pinnus*

[1] The protective duty on manufactured wares was 50 per cent. *ad valorem* in 1883, while it rose to 75 per cent. in 1897, and later to 90 per cent. In 1882 there were only 8000 power-looms (including 2500 for ribbon) and 3100 hand-looms for silk in the United States, while in 1901 the number of power-looms was 52,000 (7000 for ribbon) and that of hand-looms was reduced to 800. In the same period the number of spindles for twisting and spinning increased from 450,000 to 1,900,000. The output of silk gloves was 2000 dozens in 1887 and more than 180,000 dozens (£200,000) in 1901. The production of silk articles increased sixtyfold during the latter half of the nineteenth century.

The output in America is, however, not equal to the consumption, the proportion between them being 67·3 per cent. for silk fabrics, 85 per cent. for ribbons, and 53 per cent. for velvet. In 1901 the United States imported silk wares to the value of £5,760,000, later diminished to £3,200,000—43 per cent. from France, 18 per cent. from Japan, 17 per cent. from Germany, and 16 per cent. from Switzerland. The American Government have several times, by offering prizes, attempted to initiate the cultivation of mulberries and the rearing of silkworms, but with poor success, probably because skilled agricultural labour is lacking and is not easy to form rapidly, and also because labour is expensive.

The attempts which have been made in the Argentine have been somewhat more successful but not altogether satisfactory. To the 800,000 mulberry-trees planted during the course of 20 years, 4,000,000 have been added during the past four years, and in 1907 the crop of cocoons was 250 quintals.

nobilis), 30 to 40 cm. long and 15 to 20 cm. broad, attached to the rocks of the Red Sea and the Mediterranean (Sicily, Sardinia, Elba). It has a pale golden, more or less brownish colour, and sometimes shows greenish reflection. After being washed with soap and water and dried in the shade, it is combed and spun like other textile fibres. Although sometimes regarded as an abundant product, it is in reality rare, at least in Italy, and figures rather in museums than on the market.

ARTIFICIAL SILK is the inaccurate name given to the product which has been for some time on the market in competition with natural silk. There is, indeed, no chemical relation between the two products. In place of the fibroin and sericin produced by *Bombyx mori*, the new silvery thread contains merely cellulose, as is the case with so many other vegetable products. It has, however, the lustrous appearance of natural silk and only by reason of this property does it compete with the latter.[1]

The struggle between the natural and the artificial product has scarcely begun and it is not easy to foretell within what time and what limits the one or the other will be victorious. We are certainly on the eve of neither a serious convulsion in the agricultural industry nor the disappearance of the mulberry and silkworm, but it may be affirmed that artificial silk has established a position in the making of certain fabrics formerly obtained solely from the natural product.

The new artificial fibre has still, however, many defects which limit its use, *for the present*, to definite branches of the textile industry, and time is thus given to the producers of natural silk to repair the grave error, committed in the past, of spoiling their valuable product by excessive weighting, and so injuring its sale.

The first beneficial effect of the appearance of artificial silk should hence be to bring the silk industry to the sound basis on which it was built, and which would enable it to withstand any artificial competitor for many years to come.

The prime material for the preparation of artificial silk is cellulose, that remarkable substance which has so simple a composition—carbon, hydrogen, and oxygen—but so complex and highly polymerised a molecule (*see* p. 598), and already yields so many most important industrial products—from mercerised cotton to celluloid and pegamoid, from guncotton to collodion, from explosive, smokeless gelatines to alcohol, and finally to artificial silk.[2]

The struggle between the various types of artificial silk which have been placed on the market has resulted in victory for *viscose silk*, this, owing especially to its low cost, having practically displaced all others.

Of the hundreds of patented processes for preparing artificial silk from cellulose, most are of no practical importance and but few require mention.[3]

[1] Artificial silk, although of recent preparation, has already an interesting history. As early as 1734 Réaumur foresaw the possibility of preparing lustrous fibres, similar to silk, from gummy or adhesive substances, and in 1885 Audemars (of Lausanne) attempted but with imperfect success to put Réaumur's idea into practice.

Expectation of success in the solution of this important problem arose only later when it was found possible to prepare slender collodion fibres for the manufacture of the carbon filaments of incandescence electric lamps. In 1885 Count Hilaire de Chardonnet of Besançon, then a student at the Paris Polytechnic, filed a patent for the manufacture of artificial silk by spinning collodion solutions, and at the Paris Exhibition of 1889 he showed his first machine working. Swan, in London, had previously obtained fibres of artificial silk, but these were without practical industrial results.

[2] When cellulose is in the form of wood for fuel, 1 cu. metre cost (pre-war) about 6*s.*; the same cubic metre of wood, when boiled with lime, soda, and sulphite gives a paper pulp worth about 32*s.* and yielding paper valued at 56*s.*, or more. If this pulp is transformed into artificial silk, its value may be as high as £80 to £240, according to the articles prepared (artificial hair and silk, cellulose acetate).

[3] (1) *Nitrocellulose silk*, obtained by the denitration of collodion cotton previously dissolved in a mixture of alcohol and ether and then reduced to very fine fibres by means of special spinning machinery (de Chardonnet, Lehner, Viviers).

In 1891 de Chardonnet formed a company at Besançon with a capital of £240,000, for the manufacture of this new product on a large scale, but for some years de Chardonnet silk could not be used, as it was composed of nitrocellulose, and hence highly dangerous to the wearer and to warehouses in which it was stored, owing to its inflammability. Attempts to render the silk harmless by the addition of various substances proved futile, and the problem was solved subsequently to 1893 by the elimination of the nitro-groups combined with the cellulose by treatment with alkali hydrosulphides and the regeneration of the cellulose without alteration of its lustre; its strength, especially when wet, is, however, diminished by one-third. When treated in this way it burns almost like other cotton. After denitration, hydrated oxycellulose remains.

To obtain Chardonnet silk, collodion-cotton is prepared in the way described in the section

VISCOSE SILK. In 1892 (Eng. Pat. 8700; Ger. Pat. 70,999, of Jan. 13, 1893) E. J. Bevan, C. F. Cross and C. Beadle, by treating ordinary paper cellulose with caustic soda

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on Explosives (pp. 286, 294), and after elimination of the acid by thorough washing, the cotton is pressed hydraulically or centrifuged to reduce the moisture-content to 25 to 30 per cent. In this condition it is dissolved in 5 to 10 times its weight of a mixture of 3 parts of ether and 2 of alcohol, with which it is shaken for a couple of hours in revolving iron drums; de Chardonnet first prepared solutions of collodion with dried nitrocellulose, but found later (Ger. Pat. 16,932, 1910) that moist nitrocellulose also dissolves in alcohol and ether, avoiding the danger of drying and also giving a more homogeneous fibre. If a little mineral acid is added to the collodion solution (Lehner) the mass becomes much more fluid and requires less pressure for spinning [according to Eng. Pat. 16,932 of 1910, acetylene tetrachloride (*see* p. 122) is an excellent solvent for nitrocellulose]. The dense collodion solution is passed under a pressure of 40 atmos. through a cotton-wool filter, then left for a couple of days for the air-bubbles to escape, and finally forced first through cotton-wool and then through capillary glass tubes having a bore of 0·2 to 0·08 mm., under a pressure of 60 to 80 atmos.

The slender threads issuing from the capillary tubes under pressure and in a closed-in machine, through which a current of air passes to carry off the alcohol and ether vapour (recovered as described in Note, p. 231), are united in a number varying from 6 to 20, and under a water-jet are wound on glass spools in a coagulated condition, but still somewhat adhesive owing to the moisture left in the nitrocellulose. After a short time on these spools the fibre solidifies completely and can be manipulated without danger of the filaments adhering. It is then combined, twisted, and reeled in the same way as silk.

Denitration is effected by treating the moist skeins with hydrosulphides of calcium (0·4 to 0·5 per cent. solution) or magnesium, or, better, with dilute sodium sulphide solution for three

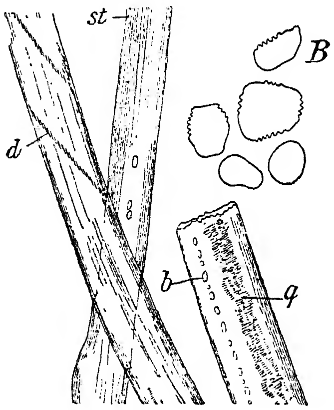

FIG. 489.—(Pauly) *d*, sign of crossed fibres; *st*, striation; *b*, air-bubbles; *q*, fine transverse striations; *B*, sections of fibres.

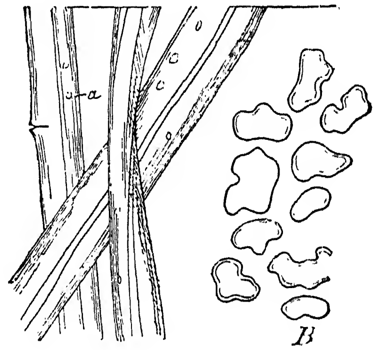

FIG. 490.—(Chardonnet) *a*, air-bubbles; *B*, sections of fibres.

to four hours in the cold. The denitration must be carried out with great care since otherwise irregular striations are obtained on dyeing. In practice all but 0·05 per cent. of N can be eliminated; this small amount of nitrogen is detectable by the diphenylamine reaction (Vol. I., p. 234, footnote), and thus allows of the distinction of this artificial silk from other silks, both artificial and natural. Artificial silks may also be distinguished from natural silk by microscopic examination (*see* Figs. 489, 490).

In 1921 the most important factory in Europe making Chardonnet silk was that of Tubize (Belgium), with a production of more than 3000 kilos per day. It is possible that this works may continue to flourish, as it produces excellent silk, especially for weaving, and also fine yarns (50 denari, whereas 120 denari is a common count for viscose silk); further, its plant is written off, it has cheap alcohol and ether at its disposal, and it obtains high prices. If, however, the latter fell, it could not survive.

(2) *Glanzstoff*, prepared by passing hydrocellulose (mercerised cotton) dissolved in ammoniacal copper oxide solution, through very fine capillary glass tubes so as to obtain—after complete coagulation in a bath of sulphuric acid at 16° to 20° Bé. or one of 5 per cent. caustic soda—filaments so slender that 225,000 metres do not weigh 1 kilo (Pauly or Fremery and Urban silk).

The first patent for this process was that of Despeissis in 1890, but this was not renewed in a year's time. The process was improved and rendered practicable by Pauly, Bronnert, Fremery, and Urban, and the manufacture was undertaken by the Vereinigten-Glanzstoff Fabriken of Elberfeld. Well defatted, bleached cotton waste is lixiviated with sodium carbonate and hydroxide in an autoclave for 3 to 4 hours, rinsed, bleached with cold hypochlorite solution, well washed and centrifuged. The mass is then treated with concentrated caustic

(which produces sodio-cellulose),[1] and then dissolving in carbon disulphide, obtained a dense, viscous, orange-yellow solution of cellulose sodioxanthate or sodio-cellulose xanthate or sodio-cellulose dithiocarbonate: $C_6H_{10}O_5 + 2NaOH + CS_2 = H_2O + NaS \cdot CS \cdot O \cdot C_6H_9O_4 \cdot NaOH$, the composition of which is analogous to that of sodium xanthate formed when sodium alkoxide is treated with CS_2: $CS_2 + C_2H_5 \cdot ONa = NaS \cdot CS \cdot OC_2H_5$.

In alkaline solution this substance constitutes the so-called *viscose*, but the molecule gradually polymerises and becomes continually poorer in sulphur owing to the separation of the complexes $S : C \cdot SNa$ and the formation of more and more highly condensed molecules, $NaS \cdot CS \cdot O(C_6H_9O_4)_2OH$, $NaS \cdot CS \cdot O(C_6H_9O_4)_3(OH)_2$, $NaS \cdot CS \cdot O(C_6H_9O_4)_4(OH)_3$, and even higher polymerides (Ger. Pat. 187,369 of 1904; 92,590 of 1896, and Fr. Pat. 334,636 of 1904). This process is the so-called *maturation* of the viscose.[2] After 24 hours at 15° the cellulose complex C_{12} . . . is formed and the viscose is soluble in water; after 6 to 7 days the complex becomes C_{24} . . . and the viscose is then soluble no longer in water but only in excess of alkali, and is readily coagulable on neutralisation with dilute acid; with less dilute acid or after the lapse of a longer time the viscose decomposes giving insoluble cellulose hydrate. These last changes occur readily and rapidly during the spinning process, so that there remains finally a slender thread of lustrous cellulose, moderately strong and elastic. During the coagulation (*see later*) of the filament, the impurities remain dissolved and are eliminated.

For the coagulation, Stearn (Ger. Pat. 108,511 of 1898) used a solution of an ammonium salt, particularly the chloride. Numerous mixtures of salts were subsequently patented, the problem being solved by the use of more or less acid solutions of sodium sulphate or

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soda to mercerise it and form sodio-cellulose, which is more soluble than cellulose in the cupro-ammoniacal liquid (6 to 7 kilos of cotton per 100 litres of solution). The latter is prepared beforehand in large tanks (in cellars) containing scrap copper and concentrated ammonia solution kept in circulation by a pump which also injects air until each litre of solution contains about 15 grms. of dissolved copper. In this liquid, stirred now and then, cellulose dissolves in six to eight days, the solubility increasing as the amount of copper present increases and as the temperature is lowered (between 0° and 4°). As soon as the cellulose has dissolved and the mass become dense and stringy it must be filtered under pressure, since if this is delayed two or three days the cellulose begins to undergo depolymerisation (especially in a warm place), and the mass loses its viscosity, with the result that the silk obtained is of poor quality, irregular and weak.

Spinning follows closely on filtration. The threads from the capillary glass tubes were at one time coagulated by passing them into sulphuric acid of about 20° Bé., but there is then danger of weakening of the fibre owing to excessive hydration, which is facilitated by the rise of temperature caused by the neutralisation of the ammonia. On this account it is now preferred to produce coagulation by means of 5 per cent. caustic soda, this giving a softer and more lustrous silk from which a very weak sulphuric acid bath readily eliminates the traces of copper hydrate precipitated by the soda. According to Ger. Pat. 221,041 (1908) coagulation with alkaline sulphite or bisulphite solution appears advantageous.

Glanzstoff competed for some years with nitrocellulose silk, but it has now succumbed in favour of viscose silk, which is cheaper and possibly superior.

(3) The silk prepared from *cellulose acetate* by Cross and Bevan seems to be free from the defects mentioned above and to be superior to all other artificial silks in its strength, which is equal to that of natural silk. The manufacture of this was started some years ago by Count Donnersmark, using acetic anhydride and chloroform, but it is too costly to compete with other silks, and is dyed only in dilute alcoholic solutions (Ger. Pat. 152,432). Excellent solvents for cellulose acetate have been found in tetrachloroethane and formic acid (Ger. Pat. 237,718 of 1907).

(4) Millar and Hummel's *Vandura silk*, obtained from gelatine solution and now from casein is not used practically.

(5) K. Hofmann (Ger. Pat. 227,198 of 1909) obtains artificial silk and also hair and films by dissolving cellulose at 220° in a mixture of concentrated phosphoric and acetic acids, and then precipitating with water or salt or alkali solution.

(6) According to a Dutch patent of 1911 (No. 431,052), part of the casein suited to the manufacture can be separated by precipitating the unsuitable casein (which gives brittle products) from skim-milk by means of sodium pyrophosphate solution (3 grms. of the salt per litre of milk). From the decanted liquid, the soluble part of the casein is then precipitated by means of dilute acid. This precipitate is pressed, dissolved in a little dilute ammonia, filtered, reprecipitated with acid, again pressed, rendered plastic with a little ammonia, and spun; the thread is rendered insoluble by means of dilute formaldehyde solution.

[1] Treatment of cellulose with a solution containing more than 12 per cent. of NaOH gives sodio-cellulose in the ratio $(C_6H_{10}O_5)_2 : 2NaOH$, which is decomposed by excess of water, giving cellulose hydrate and caustic soda; if the sodio-cellulose is treated with absolute alcohol, 1 molecule of the alkali separates, leaving *semisodio-cellulose*, $(C_6H_{10}O_5)_2,NaOH$.

[2] That the sodium atoms of the sodio-cellulose take part in the formation of viscose is shown by the fact that the sodium atoms of viscose may be eliminated by treatment with iodine solution, in accordance with the equation:

$$2NaS \cdot CS \cdot O(C_6H_9O_4)n + I_2 = 2NaI + (C_6H_9O_4)n \cdot O \cdot CS \cdot S \cdot S \cdot CS \cdot O(C_6H_9O_4)n.$$

bisulphate (Müller, Ger. Pat. 187,947, 1905). Later patents improved Müller's solution. which gave a silk of poor lustre, owing to its excessive acidity (up to 20 per cent. of free acid). The acidity necessary to produce coagulation is 1 to 5 per cent., and the greater or less rapidity of the insolubilisation depends on the quantity of sulphate, the duration of the action, and the temperature, these factors also affecting the lustre and the stickiness of the fibres (Ger. Pat. 267,731, 1911; 287,955, 1912; Fr. Pat. 449,563, 1912, etc.). In general, the acidity must be less than that of the bisulphate. The presence of glucose in the spinning bath is also advantageous.

The industrial *manufacture* of viscose silk is now carried out approximately as follows: Cellulose in sheets, as used in making paper (*see* p. 605),[1] is dried at 50° and then immersed in about 18 per cent. caustic soda solution (45 kilos or more of the solution per 15 kilos of cellulose). After 8 to 10 hours the soaked and swollen sheets are pressed hydraulically to eliminate the excess of soda, broken into lumps, and reduced in a toothed pulper to a flocculent mass. This is kept in cylinders away from the air for 4 or 5 days at 26° to 28° to allow of the complete conversion of the cellulose into sodio-cellulose.

Dithiocarbonation is effected in mixers of the Werner and Pfleiderer type (p. 472), either

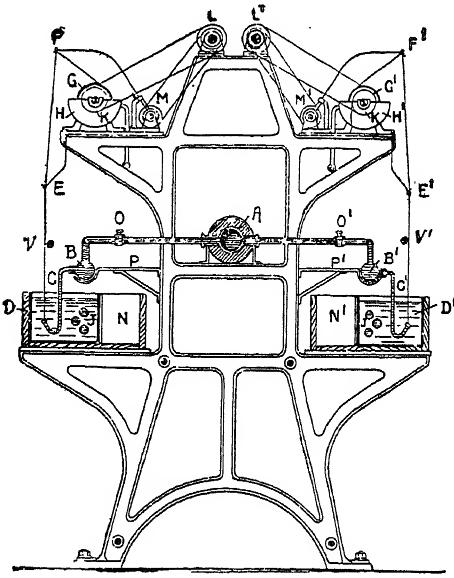

Fig. 491.

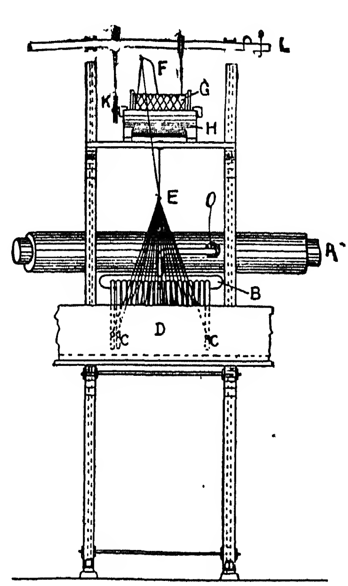

Fig. 492.

of iron or nickel-lined, with a tight-fitting cover and with a jacket for the circulating cold water. For 15 kilos of cellulose 10 to 11 kilos of pure, washed carbon disulphide is required. Mixing proceeds slowly for 2 to 3 hours, the orange-yellow, spongy, clotted mass obtained being mixed vigorously in a vertical drum with about 45 kilos of 15 per cent. caustic soda solution; sufficient water is mixed in to give a final solution of density about 1·13, corresponding with about 7·5 per cent. of cellulose and an alkalinity of about 12 per cent., expressed as NaOH. The degree of maturation required may be determined in the laboratory.

In these maturation vessels the mass (sometimes filtered beforehand through filter-presses with cloths stuffed with cotton-wool) is left at 14° to 15° for 3 to 4 (sometimes 6) days, air-bubbles and excess of carbon disulphide being expelled by prolonged evacuation of the vessels. The matured viscose solution is filtered and, clear and air-free, is conveyed to the tanks which feed the spinning machines through a pipe *A* (Fig. 491, transverse section; Fig. 492, view of front part), kept at constant temperature by means of a jacket.

[1] The cellulose should contain as little hemicellulose as possible (less than 18 per cent.), since this is not coagulated by the acid bath and is lost.

The hemicellulose is determined by heating the cellulose for an hour with 18 per cent. caustic soda solution, washing it thoroughly with hot water, drying and weighing the residual cellulose; the loss is principally hemicellulose.

The pipe, *A*, runs horizontally along the whole of the double bench carrying the two long troughs, *D* and D^1, containing the coagulating solution of density about 1·38 (at 20°) and temperature at most 55°. If the temperature in the troughs is kept between 50° and 55° the viscose filament coagulates and becomes insoluble during its passage from the mouth of the capillary tube, *C*, to the spool, *G*, which is partially immersed in a trough, *H*, containing bisulphate solution of density about 1·15 and acidity 8 per cent. at 15°.

From the main pipe, *A*, the viscose solution is pumped into the tubes, *B* and B^1, carrying thick glass tubes, *C*, terminating in a point closed with a platinum disc having 18 capillary perforations (Fig. 493). From the latter issue the slender threads (becoming far more slender on drying), which are collected into a single thread, this passing through the eye, *E*, at the rate of 40 to 50 metres per minute.[1]

The waste yarn and the lumps forming at the orifices of the capillaries when the thread breaks are thrown into the troughs, *N* and N^1. The threads are freed from part of the acid solution they hold during their passage in a stretched state past the fixed glass rods, *V* and V^1. The alteration of the acidity of the solution in the troughs by the alkaline viscose is counterbalanced by addition of fresh solution. The threads are wound crosswise on the spools to diminish their tendency to adhere.

The wound silk is washed in running water for 2 or 3 days, dried in circulating air at 65° to 70°, steamed to fix the twisting, skeined, and treated in hot dilute sodium sulphide solution to remove adherent traces of sulphur from the coagulating bath. Finally the skeins are washed in running water, bleached with dilute (*e.g.*, 0·15 per cent.) tepid calcium hypochlorite solution, softened and rendered more lustrous in a dilute sulphoricinate bath, centrifuged, and dried in a current of air at 50° to 60°. The dry skeins are beaten by hand and sorted into skeins of equal weights and hence of equal counts, those differing by more than 8 to 10 grms. per 250 grms. being discarded; with good working those discarded in this way should amount to less than 7 to 8 per cent., but with bad working they may exceed 20 per cent.

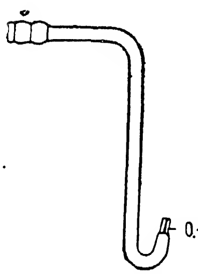

FIG. 493.

Properties, advantages and defects of artificial silk. Denitrated silk shows diminished strength and, as with other qualities of artificial silk, the strength is considerably less in the moist state; under such conditions it can still compete with heavily weighted natural silks.[2]

In general a fibre of artificial silk can be distinguished from one of natural silk owing to the small resistance of the former to tension when in the moist condition. Artificial silk is now rendered resistant to moisture and to water by treatment with formaldehyde, but this diminishes to some extent the softness and elasticity.

A further disadvantage of artificial silk is its high specific gravity, the same weight of yarn of the same size giving a larger quantity of fabric in the case of the natural silk than

[1] The machinery used in spinning artificial silk has now undergone further improvements which permit of the production at once of bundles of threads, these being subjected during their development to rapid rotation so that the completely twisted yarn is obtained in a single operation. There are also machines which give two bundles of threads twisted in opposite directions and at the same time wind the two bundles one on the other so as to produce finished organsine of two threads.

[2] According to Hassack the strengths are as follow:

	Elasticity	Tenacity in kilos per sq. mm. Dry	Moist
Natural silks boiled and lustred	20	37·5	35
,, ,, red, slightly weighted	20	20·0	15·6
,, ,, blue-black, 100 per cent. weighting	20	12·1	8·0
,, ,, black, 140 per cent. weighting	20	7·9	6·3
,, ,, ,, 500 ,, ,,	20	2·2	—
Cellulose acetate silk	17	10·2	5·8
White Chardonnet silk	9	14·1	1·7
Lehner (Frankfort) silk		17·1	4·3
Pauly (Elberfeld) silk	14	19·1	3·2
Viscose silk	14	21·5	—
Cotton thread	14	11·5	10·6

The *elasticity* is the elongation exhibited by 100 cm. of the fibre before breaking. The *tenacity* or *strength* of natural silk is 3 to 13 grms. for the single thread (bava). Echallier (Lyons) has recently increased the strength of viscose in the moist state by treating it in a bath containing 15 per cent. of formaldehyde, 5 per cent. of alum and 5 per cent. of lactic acid.

with the artificial. But while, with the first artificial silks, the excess of specific gravity was 15 to 20 per cent., the difference is now reduced to 7 to 8 per cent., and further progress in this direction is not improbable. Natural silk has the sp. gr. 1·36 and cellulose acetate silk 1·251, while other artificial silks show values exceeding 1·5.

Marked advances have been made also in the count of the thread. Until a few years ago, only yarn of 120 denari (75,000 metres per kilo) could be made, but nowadays counts of 80 denari (112,000 metres per kilo) are regularly spun, and in some cases, with Chardonnet silk, 40 denari (225,000 metres per kilo) has been reached. These are still far from the fineness of natural silk (10 to 20 denari, *i.e.*, 6 to 7 million metres per kilo), but represent an appreciable step forward. Viscose silk of 160 or even 120 denari is commonly spun.

Considerable difficulty was at first encountered in the *dyeing* of artificial silk, but nowadays the ordinary methods are used.[1]

Artificial silk of cellulose hydrate is somewhat hygroscopic and in the air absorbs 11 per cent. of moisture, whilst that with esterified hydroxyls (cellulose nitrate or acetate), like natural silk, absorbs only 3 to 5 per cent.

In its behaviour towards polarised light, artificial silk shows itself doubly refracting. By a red ammoniacal solution of ruthenium oxychloride, denitrated Chardonnet silk and viscose silk are coloured red, but non-denitrated and ammoniacal cupric oxide silk are not coloured.

When heated in a closed tube at 200°, artificial silk chars but natural silk undergoes little change.

USES OF ARTIFICIAL SILK. The most valuable property of artificial silk is its great lustre, which exceeds that of natural silk and permits of its use for a large number of different articles. Beautiful new effects are obtained by using it as weft in figured textiles with warp of natural silk, a new opening being thus provided for the latter. It is also used with advantage as weft in silk ribbons. For some years it has held almost undisputed sway in the lace industry. Fringe and cord for ornamenting garments, lace, embroidery, etc., are now largely made from artificial silk. Special articles which cannot be obtained with natural silk are made from the artificial product. There is now a large consumption of *artificial hair* prepared from artificial silk by fusing together several thin fibres so as to form a single large compact filament which, unlike large fibres obtained directly by spinning, is flexible and resistant. This artificial white hair, which can be dyed various colours, is in great demand as a substitute for horsehair, which is difficult to bleach and also rather expensive owing to the increased demand for horses for military purposes. This hair is used for various ornaments but mostly for making wigs for ladies, and artificial bristles.

Another interesting application of artificial silk is in the manufacture of incandescent gas-mantles according to Plaissetty's patent: such mantles are more resistant to shock even after burning, and can be used in trains.

Largely used also is a new product obtained from viscose, namely, a kind of *ebonite*, which serves well for the manufacture of artistically worked and coloured umbrella handles, knife handles, etc., and resists the action of the acids and alkalis with which it is likely to come into contact.

[1] When the artificial silk factories supply a *homogeneous* product, dyeing is usually accomplished without difficulty on skeins of yarn, just as with cotton and silk. The methods of dyeing are those used for cotton or, more exactly, for mercerised cotton, which is also cellulose. The dyeing can be carried out without special mordants if substantive dyestuffs (diamine, benzo, congo, etc.) are used in a bath of sodium sulphate and a little sodium carbonate at the temperature of 50° to 60°, various precautions being taken in the manipulation.

With basic dyes, a tannin or tartar emetic mordant is used, just as with cotton, the dyeing being commenced in the cold and terminated at a gentle heat in presence of 2 to 3 per cent. of acetic acid. Certain basic colours dye Chardonnet silk even without mordanting. The new sulphur colours are also used.

These different processes give all colours, from the pale and more delicate ones to black, in all shades. One merit of artificial silk is that it cannot be weighted so heavily or so easily as natural silk. Only when black can it be relatively heavily weighted.

Cellulose acetate silk is not readily dyed by aqueous solutions of colouring-matters, but as it easily fixes phenols even from dilute solution, a fine paranitraniline red can be obtained by passing the silk into a hot 0·5 per cent. β-naphthol bath and then into a 1·5 per cent. p-nitraniline hydrochloride bath containing sodium acetate. Cellulose acetate silk acquires increased affinity for colouring-matters if treated with ammonium thiocyanate.

Scroop or rustle may be conferred on artificial silk by treatment in a bath of glycerine and glucose and then in one of acetic or tartaric acid. It is freed from polysulphides by means of sodium thiosulphate.

Casein products, which have also been suggested for these purposes, cannot compete with viscose ebonite, which exhibits marked advantages over bone and horn in the manufacture of brushes, as it can be more easily worked and more easily pierced to allow of the fixing of the bristles.

As hair-ornaments for ladies, great use is made of artificial silk in thin sheets or ribbons showing brilliant colours and sparkle. Artificial silk is also used in large quantity for making materials for tapestry, upholstery, neckties, hat-linings, etc., with which no resistance to the action of water is required. With zinc salts viscose smeared on paper or fabric shows fine silky effects and fine results are also obtained with bronze powder made into a paste with viscose and spread on different cloths.

Important new outlets would offer themselves for artificial silk if the resistance to the action of water could be improved. It seems to be a question of saturating the hydroxyl groups of hydrocellulose so as to render the latter stable towards water, and the most promising attempt yet made is that with cellulose acetate, which gives a silk highly resistant but as yet too expensive, since acetic anhydride is used in its manufacture, while the cellulose acetate must be dissolved in chloroform to be spun. In America this new product is used as an electrical insulator (its *dielectric constant* is 4 and that of viscose 7, compared with 5·6 for porcelain). Other uses of cellulose acetate were mentioned on p. 599.

Numerous patents have been granted during the past ten years for the manufacture of *cinematograph films*, first from cellulose acetate (which, is, however, too elastic) and then from viscose, which is less inflammable than celluloid.

Viscose has been largely used in recent years to prepare *cellophane*, which is obtained by rendering sodium xanthate solutions insoluble by means of ammonium chloride and forming thin films (0·02 mm. thick and up to 2 kilometres in length), which are as transparent and colourless as water even when superposed to form sheets weighing from 15 to 1600 grms. per sq. metre. Cellophane is highly elastic, and its elasticity, tenacity and impermeability are increased by treating it with glycerine. It can be stamped so as to produce artistic effects. Considerable use is made of it as wrapping for sweetmeats, perfumed substances, etc., which are thus protected against water, fatty matters and gases. It resists alcohol and water even at 100°, and has been proposed as a suitable material for making cinematograph films and for rendering fabrics waterproof.

STATISTICS. The world's production of artificial silk was about 2,500,000 kilos in 1905; more than 6,000,000 kilos in 1911 (about 2,500,000 being nitrocellulose silk, an equal amount ammoniacal copper oxide silk, and nearly 1,500,000 kilos viscose silk); 7,000,000 kilos in 1913; 9,000,000 kilos (2,000,000 in France) in 1914; and probably more than 12,000,000 kilos in 1921. France exported 63,700 kilos in 1908, 78,500 in 1909, 161,700 in 1910, and 179,200 in 1911.

Italy consumes large quantities of artificial silk. Before the war the three large Italian factories (Padua, Pavia, and Turin) were working under adverse conditions owing to the excessive cost of patents and the keen foreign competition, but in 1920 and 1921 two new factories for making, like the others, viscose silk were started, with potential outputs of 3000 and 2000 kilos respectively per day. Large quantities of artificial silk are also imported.

The United States began to produce artificial silk in 1911 (150,000 kilos), and prior to the war imported large amounts from Europe. During and after the war new factories were erected, the output being 4,500,000 kilos in 1920; new plant capable of doubling this output is either complete or in course of construction.

Artificial silk, which was sold at 28*s.* to 32*s.* per kilo in 1903 and 1904, could be bought at 20*s.* in 1905, while the price fell to 16*s.* in 1906, 13*s.* 6*d.* in 1908, and 12*s.* in 1910, the poorer qualities being sold at 6*s.* to 8*s.* per kilo. The price again fell when viscose silk was put on the market and reached 8*s.* in 1913.

Even before the war many artificial silk works realised enormous profits (the dividends being 30 to 60 per cent. for some years), in spite of the huge royalties paid. Since almost all the more important patents have now expired, it is probable that this industry will undergo still greater development.

CHEMICAL TESTS FOR THE RECOGNITION OF DIFFERENT TEXTILE FIBRES

The commonest test for distinguishing animal from vegetable fibres consists in burning a thread; the former burn slowly, giving an odour of burnt nails and forming a round

granule of carbon at the point of the thread where combustion ceases, while vegetable fibres burn more rapidly, are converted into ash and give but little smell, which recalls that of burnt paper. Other reactions are as follow:

Boiling 10 *per cent. caustic potash*: Hemp, jute, flax, cotton, and artificial silk are insoluble and are not coloured (excepting jute, which becomes yellow); wool, silk, and artificial gelatine silk dissolve after a few minutes.

Cold conc. sulphuric acid (after two hours): Hemp, flax, jute, cotton, unweighted silk, and artificial silk are soluble or almost so, hemp being coloured brownish yellow, jute brownish black, and mercerised cotton yellowish, while the rest remain colourless. Wool and weighted silk do not dissolve.

Boiling zinc chloride (60° Bé): Flax, hemp, jute, and cotton are insoluble, jute alone being coloured a faint brown. Wool, silk and artificial silk are soluble.

Schweitzer's reagent (*see* p. 599), after two hours in the cold, dissolves more or less completely (better if freshly prepared), hemp, flax, jute, cotton, unweighted silk (in less than an hour) and artificial silk. Wool is insoluble.

Millon's reagent (solution of mercury in an equal weight of nitric acid of sp. gr. 1·41, first cold, then heated gently, diluted with double the volume of water and decanted after standing): Cotton, flax, hemp, and Chardonnet-Lehner artificial silk are not coloured; jute is turned yellow, wool and pure silk violet-red, and weighted silk and tussah silk ochre-red.

Conc. aqueous magenta (just decolorised with NaOH): Wool and silk are coloured red, whilst cotton and flax remain uncoloured.

Silver nitrate solution: Wool is coloured violet to black, whilst cotton and flax are not coloured.

Iodo-zinc chloride solution (1 part iodine + 5KI + 30 fused $ZnCl_2$ + 14 water) in the cold: Flax, hemp, cotton, and artificial silk are coloured violet-brown (mercerised cotton almost black); jute, wool, and tussah silk are turned yellowish and with time become colourless; true silk is not coloured.

Löwe's reagent (shake 10 grms. copper sulphate, 100 c.c. of water, and 5 grms. of pure glycerine and add caustic potash in quantity scarcely sufficient to redissolve the precipitate formed) in the cold dissolves only natural silk and is used for the quantitative separation of natural from artificial silk.

Diphenylamine sulphate (1 grm. in 100 c.c. conc. H_2SO_4) in the cold: Hemp, flax, jute, and tussah silk are dissolved, giving more or less intense brown colorations (flax dissolves less easily and is less coloured); cotton and wool dissolve with yellow coloration; silk dissolves, giving a colourless or faintly brown solution; *artificial silk* assumes an intense, characteristic blue colour.

Molisch's reagent (obtained by dissolving 15 grms. of α-naphthol in 100 c.c. alcohol): the fibre, dyed or otherwise, is first purified by boiling with 2 per cent. sodium carbonate solution and washing thoroughly with water. One centigramme of the fibre is treated with 1 c.c. of water, 2 drops of Molisch's reagent, and 1 c.c. of conc. H_2SO_4; all the vegetable fibres, including artificial silk, dissolve with a violet-blue coloration; wool is insoluble and is coloured reddish; silk is dissolved, giving a reddish (or, if weighted, an intense red) solution; tussah silk dissolves, yielding a yellowish solution.

Iodine solution (1 grm. KI, 100 c.c. H_2O, and excess of iodine): 0·1 grm. of the white fibre, purified as above with sodium carbonate, is treated with a few drops of iodine solution, the excess being removed by means of filter-paper; hemp, flax, cotton, and artificial silk are coloured blackish brown (flax more intensely than hemp and unmercerised cotton reddish brown); wool and silk become orange-yellow and jute reddish yellow.

QUANTITATIVE ANALYSIS OF MIXTURES OF TEXTILE FIBRES

It is often of importance for trade or fiscal purposes to determine quantitatively substances extraneous to textile fibres in order to ascertain their *commercial weight*. This is determined by means of the so-called conditioning.

In *conditioning*, which is now carried out officially, the moisture is estimated by drying in an oven with automatic regulation, and thus determining very exactly the amount of dry fibre (absolute weight) remaining after silk has been heated at 120° or wool and cotton

at 105° to 110°. To obtain the commercial weight the absolute weight is increased by the normal moisture which the hygroscopic fibre absorbs from the air, this being fixed at 12 per cent. for *flax* and *hemp*, 13·75 per cent. for *jute*, 8·5 per cent. for *cotton*, 18·25 per cent. for combed *wool*, 17 per cent. for spun and carded wool, and 11 per cent. for *silk* (120°); also the amount of dressing in the fibre must be deducted. It is, however, to be noted that usually wool has only 11 per cent., silk 8·5 per cent., and cotton 7·5 per cent. of moisture when in ordinary surroundings.

Dressing: 5 grms. of the fabric are well washed with water, wrung out, boiled for 15 minutes in 150 c.c. of 0·1 per cent. sodium carbonate solution, washed in water and rubbed—all the fibres being grasped—heated to boiling with 150 c.c. of 1 per cent. HCl and kept on the steam-bath for 15 minutes, again washed and rubbed, boiled for 15 minutes with distilled water, washed with cold water, pressed in a towel, washed two or three times with alcohol and two or three times with ether, dried in the air and then in an oven to constant weight.

The loss in weight, after allowing for the moisture (*see* preceding determination) represents the dressing and colouring-matter; the latter is almost always a negligible quantity, but in the case of black may be taken at about 0·3 per cent. of the weight of the pure fibre.

Mixed Cotton and Wool Fabric. After the moisture and dressing have been determined, the cotton may be estimated and the wool deduced by difference or *vice versa*. The cotton is determined by boiling 3 grms. of yarn or fabric with 100 c.c. of 10 per cent. caustic potash solution, the wool quickly dissolving; the residue is well washed with water, boiled for 15 minutes with distilled water, squeezed, washed with alcohol and with ether, and finally heated at 100° to 105° until of constant weight, representing the dry cotton. In reducing this to percentage, account is taken of the moisture and of the dressing. If, however, the wool is to be determined directly and the cotton by difference, 3 grms. of the fabric are boiled for 15 minutes with 0·1 per cent. sodium carbonate solution, rinsed in water, well wrung out in a towel and left for two hours in cold sulphuric acid of 58° Bé.; it is then washed in a large amount of water—care being taken that the remaining wool does not become heated—boiled for 15 minutes in distilled water, squeezed, washed with alcohol and with ether, and dried at 100° to 105° until of constant weight, which represents the dry wool.

Mixed Cotton and Silk Fabric. After the moisture and dressing have been determined (*see above*), the same piece of dried fabric is immersed for a minute in a boiling solution of zinc chloride (60° Bé.) and washed first with water slightly acidified with HNO_3 and then with pure water until the wash water gives no zinc precipitate with ammonium sulphide, the remaining *cotton* being washed with alcohol and with ether and dried at 100° to 105° until of constant weight; the silk is calculated by difference. In the case of tussah silk, the action of the zinc chloride is prolonged somewhat. In order that no loss may occur with a heavily weighted silk, the dressing is eliminated by means of sodium carbonate alone, treatment with hydrochloric acid being omitted.

Mixed Wool and Silk Fabric. The silk is dissolved in zinc chloride and the residual wool weighed, the silk being determined by difference (*see above*).

Natural and Artificial Silk Fabric. The natural silk is dissolved in Löwe's reagent (*see above*).

Cotton and Linen Fabric. As a rule the different fibres can be separated by hand, but when this is not possible the cotton (after the moisture and dressing have been determined on the same piece of fabric) is dissolved by immersing the tissue for 1 to 2 minutes in concentrated sulphuric acid; the fibre is washed well with water—being rubbed meanwhile—then with water and ammonia, and again with water, the linen remaining being dried and weighed. The cotton is obtained by difference.

Different Artificial Silks. Those from nitrocellulose (Chardonnet, Lehner, etc.) contain traces of nitro-derivatives and with diphenylamine and sulphuric acid give a blue reaction, which is not shown by other silks. P. Maschner (1910) distinguishes different silks by treatment with concentrated H_2SO_4; that from nitrocellulose colours the liquid a faint yellow only after 40 to 60 minutes; ammoniacal copper oxide silk is coloured yellow or brownish yellow immediately, while the liquid becomes brownish yellow after 40 to 60 minutes; viscose is at once coloured carmine-red, the liquid turning brown after 40 to 60 minutes. The fibres dissolve after about 20 minutes and then carbonise.

DYEING AND PRINTING TESTS ON TEXTILE FIBRES

Of some importance are the tests which admit of the classification of colouring-matters according to their basic, acid, neutral, or mordant character. To this end, dyeing or printing tests are made on a small scale with wool and cotton (*see also* p. 795 *et seq.*). Tests made with *colorimeters*, which compare the intensities of coloration of solutions in tubes of equal lengths or vessels of equal thickness, are of little practical value. Hence to ascertain the dyeing power of any commercial product, the latter is compared with a standard colouring-matter by weighing out equal quantities (0·1 to 1 grm. per litre of water) of the two, and dyeing equal weights of wool, cotton, or silk fabric with definite volumes of the more or less diluted solutions. The quantity of dye used is always referred to the weight of the fabric, independently of the dilution of the bath; this is especially the case with wool (0·1 per cent. of the dye for pale colours and 2 to 4 per cent. for dark colours). The dyeing tests are made on 1 to 2 grms. of wool or cotton yarn or tissue in glass or porcelain beakers of 150 to 250 c.c. capacity, these being heated in a bath of concentrated sodium sulphate solution or of glycerine giving a temperature of 101° to 102° in the dye-bath (*see* Fig. 494).

If the bath retains much colour after the dyeing, a second portion of the textile is dyed without adding fresh dye. If the cotton is raw it must first be boiled for an hour in a 0·5 per cent. caustic soda solution, and then thoroughly rinsed with water. If light colours are used, the cotton is also bleached in calcium hypochlorite solution (less than 1° Bé.) at 25° to 35° for an hour, washed with water, immersed in a 1 per cent. sodium bisulphite bath (*antichlor*), and well rinsed in water. Wool, if impure, is heated at 60° for 10 minutes with a solution containing 0·5 per cent. of soap and 0·1 per cent. of sodium carbonate, and then well rinsed with water. Also silk, if not already discharged, is washed with hot soap solution.

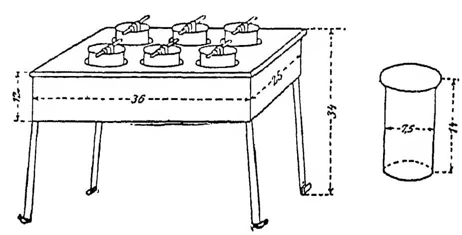

FIG. 494.

The comparative dyeing tests should be made on equal quantities of textile fibre wetted uniformly before introduction into the dyeing bath. Silk is dyed like wool, but the bath is made less acid and the temperature rather lower. Wool is dyed in an aqueous bath containing 10 to 15 per cent. of sodium sulphate and 5 per cent. of sulphuric acid (or 6 to 7 per cent. of sodium bisulphate—the German *Weinsteinpreparat*—in place of the sulphuric acid) calculated on the weight of fibre; the bath is stirred continually with a glass rod and heated gently to boiling, being kept slowly boiling for 20 to 30 minutes; the wool is then rinsed and dried either in the air or in a water-oven. The above procedure is followed more especially for acid dyes; with basic dyes, one-quarter of the amount of sulphuric acid is sufficient. When wool is dyed with acid dyes, it is not merely necessary to add to the dye-bath the quantity of sulphuric acid required to liberate the acid residue of the dye so that this can be fixed on the wool, but in order that the latter may be dyed intensely and well, 20 to 30 times the theoretical amount of sulphuric acid must be added (E. Knecht, 1888). With mordant dyes, the *wool is mordanted* with 3 per cent. of potassium dichromate and 2·5 per cent. of cream of tartar (on the weight of wool) and about 100 times the weight of water, heating gradually to boiling and maintaining this for nearly an hour, the water evaporated being gradually replaced; the wool is then rinsed and dyed in the dye-bath, which contains a little acetic acid (1 per cent. on the fibre), and is mixed continuously and brought slowly to the boil, boiling being maintained for about an hour.

Knecht and Hibbert (1903–1905) determine the concentration of the colouring-matters in the different solutions by reduction with standard titanium trichloride solution; crystal violet, for example, fixes 2H, giving the colourless leuco-derivative.

Cotton is dyed with *substantive dyes* in more concentrated baths (50 of water to 1 of cotton) containing 30 to 50 per cent. of sodium chloride or sulphate and 1 to 2 per cent. of sodium carbonate (on the weight of fibre); this is heated slowly and kept boiling for 30 to 40 minutes; in general the bath is not exhausted and can be used for a second portion of cotton. In the case of *sulphur colours*, 20 to 30 per cent. of sodium sulphide are added to the bath and in some cases 2 to 3 per cent. of glucose, and during the dyeing the cotton is kept immersed and out of contact with the air. When *basic colouring-matters* are used the

cotton is previously mordanted with 2 to 4 per cent. of tannin dissolved in water, being left in contact with this solution for 6 to 7 hours (overnight) at 50° to 60° (the tannin is fixed more slowly in the cold); the cotton is then wrung, immersed for 10 minutes in a bath containing 2 per cent. of tartar emetic (antimony potassium tartrate) at 40°, rinsed with water and dyed in the tepid (30° to 40°) dye-bath for 20 to 30 minutes.

Dyeing on a large scale is carried on under the same conditions, but the calculations are made on a longer time, and great precautions are taken in the moving of the fibre and in raising the temperature, so as to obtain uniformity. For dark colours, the tannin is fixed with ferric nitrate instead of with tartar emetic. Industrial dyeing apparatus is shown more in detail later (p. 841).

PRINTING TESTS. The object of printing is to colour the fabric or yarn in a definite pattern or with different colours, part of the fibre being possibly left unaltered. In the first rudimentary printing processes, the fabric was printed with resin or a kind of cement, the uncovered parts being dyed as usual and the preserving substance subsequently removed. It is now usually regarded as preferable to stamp, *i.e.*, to print, on the fabric or yarn the colour mixed with *thickening* (gum, dextrin, gum tragacanth, etc.) by means of metal rolls on which the desired pattern is engraved. The engraved roll is coated with the pasty colour by rotating against a rubber or cloth roller (*furnisher*), one-half of which dips in a vessel containing the thickened colour; a knife (*doctor*) is arranged so as to scrape the excess of colour from the metal roll, and the yarn or fabric then passes over the latter under pressure. In order to fix the colour and prevent it from spreading, the fibre is subjected for 30 to 60 minutes to the action of steam at about 105° (*see* Fig. 552, p. 855). By this means the colour is fixed without immersing the printed fibre. The latter is subsequently washed with an abundance of cold water (or with tepid soap and water), which removes all excess of colour and thickening agent. In other cases similar effects are obtained by dyeing uniformly in the ordinary way and then printing on the dyed fabric reagents which decolorise (corrode) the dye at the points of contact. Sometimes other colours are introduced with the corroding agent, so that the white parts are dyed a lighter or darker shade or a different colour from the foundation.

A kilo of thickened colour for printing wool black—the wool having been previously subjected to slight chlorination to make it take up the colouring-matter better (by immersion in a cold calcium hypochlorite bath at 0·5° Bé. and then in very dilute HCl, washing, and drying)—may be obtained as follows: 750 c.c. of water, 100 grms. of gum, and 100 grms. of *British gum* (dextrin) are heated in a jacketed vessel by means of indirect steam and kept well mixed, 60 grms. of anthracite black E G and 10 grms. of milling yellow O (and, in some cases, 8 grms. of acid anthracene brown R) being added. When the paste is boiled uniform, it is allowed to cool, and before it is used a solution containing 80 c.c. of water, 120 c.c. of acetic acid (6° Bé.), and 40 grms. of sodium chlorate is well mixed in.

For printing cotton textiles, colours are used which form insoluble lakes with tannin or metallic oxides; such are basic and mordant colouring-matters (alizarin, etc.). The former are dissolved in acetic acid and tannin (or a solution of 50 parts of tannin, 50 of water, and 5 of tartaric acid) and the latter (alizarin, etc.) in chromium (or iron, aluminium, etc.) acetate, dextrin, gum, etc., being added in either case. Fabrics treated with tannin, after being steamed at the ordinary pressure and before being washed, are passed into a bath containing 5 to 10 grms. of tartar emetic per litre at 60°.

FASTNESS TESTS. The fastness of a colour is only relative and must be considered with reference to the purposes for which the dyed fibre is required; for example, it would be superfluous to require fastness against light in dyed fibres or fabrics to be used for underclothing, linings, etc. The dyed specimen is mixed with similar undyed fibre and subjected to the following tests, as required. Mordanted colours answer all these tests fairly well, but in other cases more or less of the colour is given up.

Fastness against Water. The sample is immersed in 50 times its weight of cold water for 12 hours or for 1 hour in water at 60° to 70° (and is left to cool in the bath) and is then dried in the oven. Note is taken of the colour assumed by the water and by the white fibre, especially where the latter comes into contact with the dyed fibre.

Fastness against Soap, Alkali, and Washing. The skein of white and dyed fibre is immersed in 50 times its weight of an aqueous solution containing 10 grms. of Marseilles soap and 10 grms. of soda per litre. The bath is heated at 60° for 30 minutes and allowed to cool, the skein being then removed, well rinsed, and dried. The changes in colour of the bath and the white and dyed fibres are observed.

Fastness against Milling. This test is carried out with a soap and soda solution, of double the above concentration, at 40°, the skein being continually rubbed between the hands for 30 minutes, and then well washed and dried in the oven. Colours fast to milling should not soil the white portion of the skein and should give up only a minimal amount of colour to the bath.

Fastness against Bleach. If the colour is on wool or silk it is immersed in a 2 per cent. sodium bisulphite bath acidified at the moment of using with a few drops of hydrochloric acid, and, after 30 minutes, washed and dried. When the colour is on cotton, the test is made with a calcium hypochlorite bath at 0·5° Bé. for half an hour.

Fastness against Scouring. Indigo, Turkey-red, and all basic dyes on cotton mordanted with tannin, even when dry, give up a little colour to a white handkerchief with which they are scoured. Other dyes should not soil the white.

Fastness against Acid. The test is carried out for an hour with 1 per cent. sulphuric acid at 60° to 70°.

Fastness against Perspiration. In some cases this test is made with a 1 per cent. acetic acid solution for 30 minutes at 40°, the skein being dried at 60° under slight pressure, without rinsing and after thorough rubbing. In others, an alkaline test is made—as in testing fastness against washing—but the unrinsed skein is subsequently scrubbed and dried at 60° under slight pressure.

Fastness against Ironing. The dyed fabric or yarn is ironed with a very hot iron (130° to 140°), note being taken whether, after cooling and exposure to the air for 15 minutes the fabric resumes its original colour. Many colours are changed by ironing hot, but return to their initial state in the cold.

Fastness against Steaming. The yarn is placed in a glass tube, through which steam at 110° is passed for two or three minutes.

Fastness against Light. One half of a skein of yarn or of a strip of fabric is tightly enclosed between two pieces of card, while the other half is left free; the whole is then hung in the open air exposed to the sun and weather. For pale colours, an exposure of at least two days, and for dark colours, one of at least four days, is necessary in summer, while in winter or in cloudy or rainy weather (the skein must be sheltered from rain), at least double or even treble these exposures are necessary. The covered and uncovered portions are subsequently compared.

Fastness of the Dressing against Rain. A few drops of water are sprinkled on the fabric, especially finer woollen ones, and after exposure to the air it is noted whether the drops have left faint spots. In some cases the fabric is scratched with the thumb-nail; a paler streak should not result. This test is not applied to cotton fabrics strongly dressed, since the nail will sometimes detach the dressing itself.

THEORY OF DYEING. The phenomenon of dyeing was at one time thought to be due to the porosity and capillarity of fibres which were thus enabled to absorb and become impregnated with dyes. The possibility of chemical combination between the dye and the fibre was regarded as excluded, it being asserted that in such case the fibre would undergo marked change. The different colouring powers of substances were explained as due to different molecular magnitudes. Even at the beginning of last century, in Chevreul's time, these ideas prevailed, and only in the case of mordant dyeing was any chemical fixation of the dyestuff assumed. Later on, Bergman, J. Persoz, etc., arrived at a purely chemical conception of the phenomenon of dyeing, but when in 1885 substantive cotton dyestuffs of almost neutral character made their appearance, the chemical theory, which was based mainly on the basic or acidic nature of the dyestuffs, was in some degree shaken. Many then accepted a new theory in harmony with the osmotic phenomena of solutions, the more readily because no definite and constant relation between the amount of fibre and that of dyestuff combined had been established. The chemical theory was and is still, however, upheld by many authorities on the subject, more particularly by Noelting, by Knecht, and by Vignon, who have pointed out that alloys form well characterised compounds which exhibit no definite chemical relations between the components and may be regarded as true solid solutions of one substance in excess of the other. Further, they were able to show that silk and wool, in combining with colouring-matters, set free the acid united with the base of the dyestuff, this acid being found in the dye-bath. Also, with certain acid dyestuffs (*e.g.*, naphthol yellow), Knecht and Appleyard found a constant relation between fibre and dyestuff.

Jacquemin asserts that if there were no question of chemical combination, the dry

dyed tissue should have the colour of the dry colouring-matter, whereas it has the same colour as the dissolved colouring-matter. Nietzki finds that with certain highly basic colours (*e.g.*, methyl green), wool cannot of itself displace the mineral acid of the colouring base, the addition of ammonia being necessary ; while, with the same colouring-matters the more markedly acidic silk is dyed without any addition.

An interesting fact, which supports the chemical theory, is that the base of rosaniline is colourless and becomes red (magenta) only when converted into a salt with HCl ; a similar change is produced if wool is immersed in a colourless rosaniline (base) bath, the wool being dyed red owing to the formation of a salt. If the dyeing is effected directly by rosaniline hydrochloride, the bath ultimately contains the hydrochloric acid which is displaced by the acid of the wool fibre (Jacquemin and Knecht, 1888).

Moreover Richard (1888), Vignon (1890), and Nietzki (1890) showed that silk and also wool are active both towards acids and towards bases, so that in chemical characters they are comparable with the amino-acids. The fibre may even be replaced by albumin, which is dyed by the same dyestuffs as wool, etc.

According to W. Suida (1907) the dyeing of wool is accompanied by liberation of the base of the dyestuff which combines (or forms salts) with the textile fibre, the latter functioning as a polybasic acid in virtue of its guanidyl and iminazole groups. Also Vignon showed that when wool and silk are dyed with basic or acid colouring-matters heat is developed, so that the dyeing may be regarded as a true, exothermic chemical reaction. According to Vignon cotton is not dyed directly by basic or acid dyestuffs (which are usually salts) since it has not the reactive force to decompose them, but if it is previously oxidised or aminated, it fixes these dyestuffs partially with development of heat. Further, the difference in fastness against light of the same colouring-matter (*e.g.*, methylene blue) fixed on cotton (with tannin) and on wool or silk would appear to favour the chemical hypothesis of the phenomenon of dyeing.

In 1889 O. N. Witt advanced a new theory, which explains also the dyeing of cotton with substantive and mordant dyes. According to Witt, dyeing consists merely of a solution of the colouring-matter in the fibre, analogous to that of solution of coloured metallic oxides in glass, so that the colouring-matter passes from a liquid solvent (dye-bath) to a solid one—the fibre itself—just as occurs with alloys or in the extraction with ether of a substance dissolved in another solvent in which it is less soluble than in ether—assuming that the two solvents are mutually insoluble.

Dyeing on mordants is similarly explained as due to the solvent properties of the fibres for the metallic salts, these then fixing the colouring-matter from the dye-bath. The dyeing of cotton with substantive dyestuffs is regarded as the result of the marked solvent power of cotton (cellulose) for these dyes. In support of his theory, Witt cites the fact that silk dyed with magenta gives up its colour to alcohol, which is a better solvent for magenta than is silk, while if the alcohol is then diluted with water, the colour is again fixed by the silk.

To this observation Knecht (1902) made the reply that, with substantive colouring-matters lanuginic and sericinic acids form insoluble lakes, *i.e.*, true compounds, while with magenta they form lakes soluble in alcohol ; it is therefore to be supposed that the magenta extracted by Witt with alcohol is in reality the soluble lake formed by the magenta with the components of the fibre. Rosenstiehl (1894), Reisse (1896), and Gillet (1898), after various quantitative dyeing tests, decided in favour of the chemical hypothesis.

In 1894–1895 Georgievics advanced a number of arguments in favour of a purely mechanical theory of dyeing (his predecessors of a century earlier being Hellot and Le Pileur d'Apligny, and those of more recent times Walter Crum, Spohn, and Hwass). Comparing the latter with occlusion of gases by solids or with the mechanical fixation of dyes on sand or on powdered charcoal, etc., he maintained that colouring-matters fixed on fibres have the same properties as those not so fixed, and that there can hence be no question of a chemical reaction (*but see above*, Knecht's experiment), since some dyestuffs fixed on fibres can be separated by mere sublimation, while in other cases (with methylene blue and indigo carmine) the coefficient of distribution of the colouring-matter in the fibre and in the solution is constant. According to Krafft (1899), dyeing generally consists in a deposition, on or in the fibre, of adhesive and resistant colouring salts in the colloidal state.

Biltz (1905) has succeeded in producing true dyeing phenomena by replacing the textile fibre (cotton) by aluminium hydroxide or other hydroxides which behave as *hydrogels*

(*see* Vol. I., p. 106) towards the colouring-matter, which is regarded as a colloid (benzopurpurine and sulphur dyes). Freundlich and Losev (1907) have shown that carbon not only fixes colouring-matters but decomposes basic colouring-matters, fixing the coloured base in the colloidal state and leaving the acid in solution, in the same way as happens with wool or silk. Knecht has recently (1909) found that the amount of colouring-matter fixed by charcoal is related to the quantity of nitrogenous matter remaining in the charcoal even after ignition, so that here a true chemical reaction occurs; this investigator has also shown that colouring-matters cannot be regarded as colloids, since they are electrolytes and diffuse through membranes.

In 1909 Dreaper and Davis demonstrated that basic colouring-matters are fixed in constant quantity on calcined sand, and in increased quantity if the dye solution contains sodium chloride. Rosenstiehl assumes that the phenomenon of dyeing is explainable by the cohesive force between the colouring-matter and the textile fibre, this force varying with the liquid or gaseous medium in which the dyeing takes place and depending on or being produced by the osmotic pressure of this medium.

According to Müller (1909) dyeing may be regarded as a phenomenon of *adsorption* of the colouring-matter by the colloid, *i.e.*, the textile fibre. There is hence not chemical combination, but fixation under definite conditions (of moisture and temperature).

Mercerised cotton fixes colouring-matters better on account of its more marked colloidal character. The process of fixation or adsorption may also be reversible and all the phenomena of direct dyeing depend on the relative coefficient of adsorption of the colloid (fibre) for the colouring-matter. Freundlich and Losev and Pelet-Jolivet attribute dyeing to *adsorption*, because the fixation of the colouring-matter from solution by any textile fibre obeys the formula, $\frac{x}{m} = K \cdot C^{\frac{1}{n}}$ (where $\frac{x}{m}$ denotes the ratio between the quantity of colour absorbed and the weight of the textile fibre, K and $\frac{1}{n}$ are constants, and C indicates the final concentration of the colouring-matter), which also regulates the adsorption of gases by solid substances and that of various dissolved substances by animal charcoal. It cannot, however, be denied that certain limited chemical processes also correspond with this formula, and that many phenomena accompanying dyeing are most simply explained chemically.

Indeed, W. J. Müller and Slassarski (1910), by means of experiments on the dyeing of artificial silk, show that the absorbed colour varies in quantity with the chemical properties of the cellulose (raw, oxycellulose, hydrocellulose).

Every hypothesis is supported by some experimental fact, and it would seem that, according to the nature of the fibre, of the colouring-matter, and of the dyeing process, the phenomenon is explainable either on purely physical or on purely chemical grounds, but more generally on both.

O. Weber (1891, 1899) and Gnehm (1898) explain the various phenomena of dyeing in the following way: (1) Dyeing on mordanted cotton is due to the formation of lakes between the colouring-matter and the mordant precipitated mechanically on the cotton. (2) Azo-colouring-matters formed directly on the fibre (*see* p. 781) or pigments held by it (ultramarine, cinnabar, ochre, Guinea green, etc.) are merely precipitates deposited mechanically in the pores of the fibre. (3) The direct dyeing of cotton with substantive dyes consists in dissolution of the colouring salt in the cell juice, and the marked fastness against washing of these colours on cotton is due to their slow diffusion with the juice (Müller-Jacobs and Weber). (4) Dyeing of tannin-mordanted cotton with basic or indigo colours is a true mechanical occlusion. (5) Direct dyeing of wool and silk and other animal fibres with basic or acid colouring-matters is due partly to mechanical absorption, and partly to chemical combination, of the colouring-matter by the fibre. (6) The dyeing of *mordanted* animal fibres is explained by the formation of insoluble lakes, partly by the mordant fixed chemically by the fibre, and partly by that fixed mechanically within the fibre, but is never caused by combination of the unchanged fibre with the colouring-matter.

Pelet-Jolivet's *colloidal theory of electric contact*, based on Perrin's law of contact electricity also finds support. According to this theory the fibre in an alkaline bath is negatively charged and the basic colouring matter positively, neutralisation of the charges resulting in precipitation (adsorption) of one colloid on the other (the colouring-matter being assumed to be colloidal). In dyeing with acid dyestuffs, the fibre becomes positively charged by addition of acid to the bath and adsorbs the negative acid colouring-matter.

As regards the *mordanting* of wool, it has been shown that when this is boiled with metallic salts, it fixes not only the basic part but also the acid part of the salt (only of unstable salts, *e.g.*, sulphate of Al, Cr, Cu, or Fe, and not sodium sulphate or chloride); the latter part is eliminated to some extent by water, but the basic part is fixed more stably.

MACHINERY USED IN DYEING AND FINISHING TEXTILES

The limits of this treatise do not allow of the inclusion of a complete description of all the machinery used in works where textile fibres are dyed and finished. We shall hence confine ourselves to illustrating some of the principal washing, dyeing, and dressing machines.

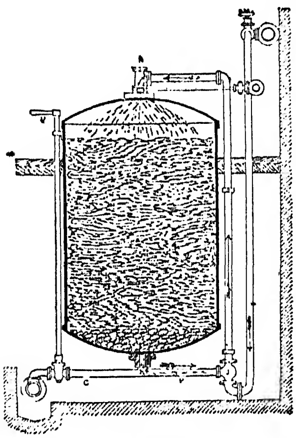

FIG. 495.

WASHING AND PREPARATION. At the dye-house, textile fibres arrive either raw (cotton and wool in flock) or combed (wool in skeins or *tops*) or spun in skeins or on bobbins (wool, cotton, silk), or more commonly woven in pieces 30 to 100 metres long and 60 to 140 cm. wide (woollen, cotton, silk, or mixed fabrics).

Wool is sometimes supplied free from its natural fat (*see* p. 805) but, whether as fabric or as yarn, contains the fat or dressing used in weaving or spinning.

Cotton is still in the raw state, and, in order that the colouring-matter may be fixed well it is subjected to energetic boiling under slight pressure with water and with soda. With either flock or skein cotton, this treatment is carried out in large, closed, iron or copper boilers (Fig. 495), provided with pumps or steam-injectors for circulating the liquid, the textile material not being moved as it might be damaged. As a rule the boiler is either evacuated or freed from air by a current of steam, since air damages the fibre owing to formation of oxycellulose, and also gives dark lye; along with the caustic soda, vigorously frothing soap (from castor oil, for example) is introduced.

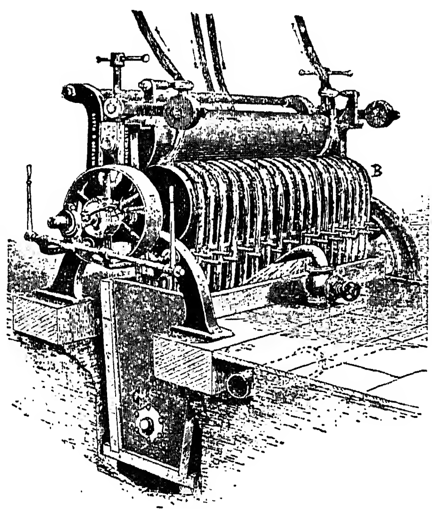

FIG. 496.

The washing of cotton goods to rid them of the starch with which the weft was charged for weaving purposes was at one time carried out by heating them with milk of lime, but better results are obtained by heating with dilute caustic soda solution in an autoclave under steam-pressure. Nowadays the goods are often passed through a lukewarm bath of *diamalt* or *diastofor* (malt extracts rich in diastase) and left in heaps overnight, the starch being thus transformed into soluble dextrin and maltose. The latter products are removed by thorough rinsing in water: the material passes between the two rollers *A* and *B* (Fig. 496) into the water, round the roller *C*, up between *A* and *B*, down again and so on until it reaches the middle, where it is removed, together with a similar piece introduced at the other end of the machine; the pieces of material are tied end to end and passed through this washer in a continuous length; an abundant supply of water enters the vessel at *D* and is drawn off through another pipe.

When washed the goods are *soured* with a solution of sulphuric acid (0·5° Bé.), either cold or tepid (with the latter the action is very rapid, even with more dilute acid); the pieces may be tied together in cords and passed through this solution (*see* Fig. 496). Bleaching is then effected in a clear chloride of lime bath (0·5 to 0·75° Bé); this occupies some hours in the cold, or, if the liquid is lukewarm, the material may be passed continuously

through it as before. Then follows rinsing and treatment with antichlor (sodium bisulphite).

Skeins of cotton yarn may also be *bleached* with chloride of lime in an apparatus with automatic circulation of the liquid, as is shown in Fig. 495, while the rinsing may be effected in rotating machines (Fig. 497), where each skein rotates on a wheel and all the reels rotate horizontally in a circulation vessel, a water-spray being used meanwhile.

According to Pick and Erban cotton may be bleached in the cold, without preliminary boiling with alkali, by means of sodium hypochlorite solution mixed with sulphoricinate; in this way, the strength of the fibre is retained better, while time is saved (Ger. Pat. 176,609 of 1906). Cotton or cotton and wool fabrics may be bleached by passing them repeatedly into a sodium permanganate bath (0·6 to 0·7 per cent. of the permanganate on the weight of fibre) until the bath is almost decolorised and the fibre turned brown, then into a sodium sulphite or sodium nitrite bath (0·6 to 0·7 per cent. on the fibre) and finally into sulphuric acid (4 per cent. on the fibre).

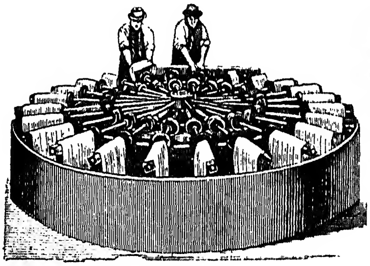

FIG. 497.

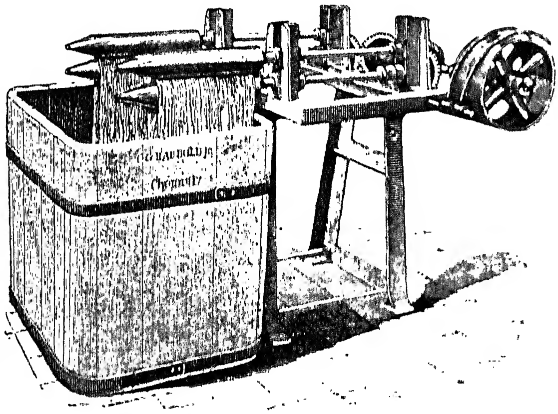

FIG. 498.

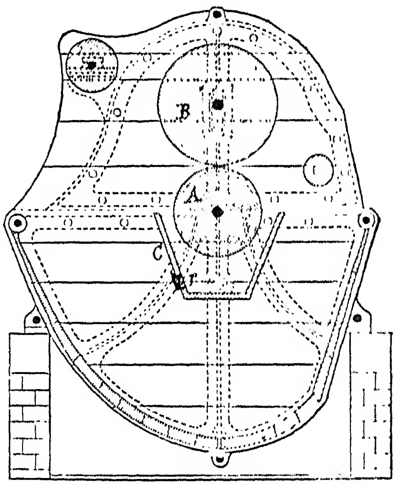

FIG. 499.

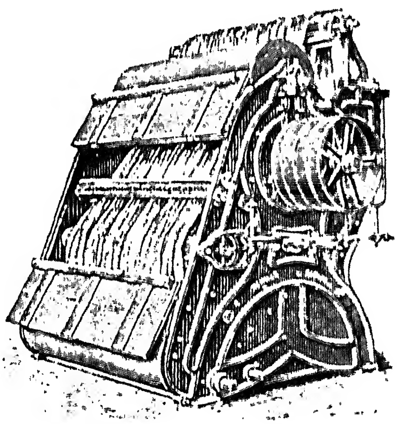

FIG. 500.

The Washing of skeins of *wool* yarn in a tepid bath (50° to 60°) is carried out by passing the skein for a minute between two rolls (Fig. 498), then twisting the skein and again squeezing it. Subsequent thorough washing with water—in the vessel shown in Fig. 497, for example—renders the skein of wool ready for dyeing. In all these operations and in those which follow, woollen yarns are treated with greater care than cotton ones, it being necessary to manipulate, press, and rub them as little as possible and only very slowly, in order to avoid felting.

Bleaching of washed woollen yarns or fabrics (wrung out uniformly by means of centri

fuges: *see* p. 566) by *sulphuring* is effected by stretching them out on rods in tightly closed chambers in which sulphur has been previously burnt in a cup situate in an angle heated by a furnace outside. Here the wool is left overnight, and in the morning the windows are opened and the wool dried and deodorised in the air. The amount of sulphur burnt is 2 to 3 per cent. on the weight of the wool, or less if the chamber is a small one, and deficiency of air is maintained in order to avoid sublimation of the sulphur and its deposition as a yellow powder in the wool.

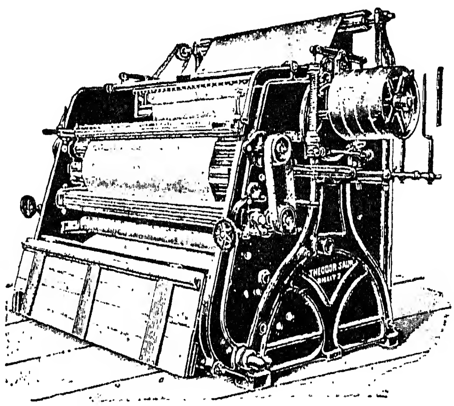

FIG. 501.

Bleaching with Hydrogen Peroxide, is carried out in the cold or at a gentle heat, and for woollen yarn, paraffin waxed wooden vessels, or, better, cement troughs, are used. Woollen or silk fabrics are wound into a vessel similar to that used for dyeing (*see later*), or, better, on a jigger (*see later*). The bath is prepared by diluting commercial 10 to 12 vol. H_2O_2 with 8 to 10 times its volume of water, and rendering it slightly alkaline with ammonia (*see* Vol. I., p. 267). After use the bath is preserved by acidification with sulphuric acid.

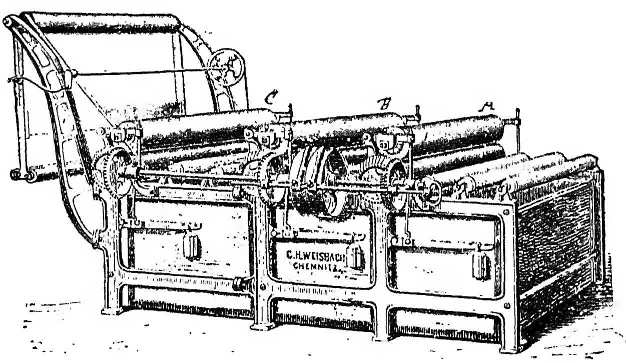

FIG. 502.

More economical bleaching is obtained with sodium peroxide, which, however, must be used with great caution (*see* Vol. I., p. 553); better results are obtained with sodium perborate (*see* Vol. I., p. 605) in a bath containing, say, 200 litres of water, 600 grms. of sulphuric acid of 66° Bé., and 1·8 kilo of sodium silicate at 40° Bé.

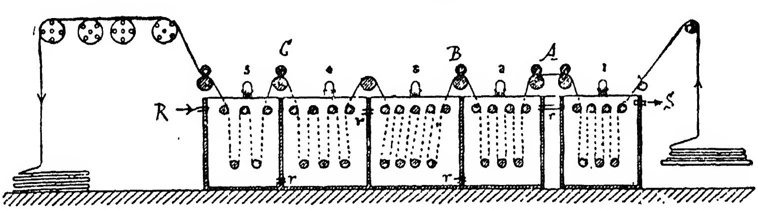

FIG. 503.

Washing of Woollen Fabrics is carried out in various ways. A number of the pieces, the two ends of each being tied together, are wound round in a trough fitted with a pair of pressure rollers, *A* and *B* (Figs. 499, 500), and containing hot soap and soda solution. Beneath the rolls is a wooden channel, *C*, to collect the expressed liquid, which for some time is allowed to run back through *r*, but when dirty is run off outside. Thorough rinsing with water is carried out in the same vessel. It must be noted that almost all washing

and dyeing machinery is fitted with arrangements for obtaining different velocities of the moving parts, with pipes for water and steam, etc.

Very heavy woollen fabrics are more easily washed at their full width in vessels (Fig. 501) similar to the preceding, but the lighter ones are most conveniently dealt with by joining the pieces end to end so as to form a single piece, which is treated in the machine shown in Fig. 502, and, in diagrammatic section, in Fig. 503. This is furnished with three pairs

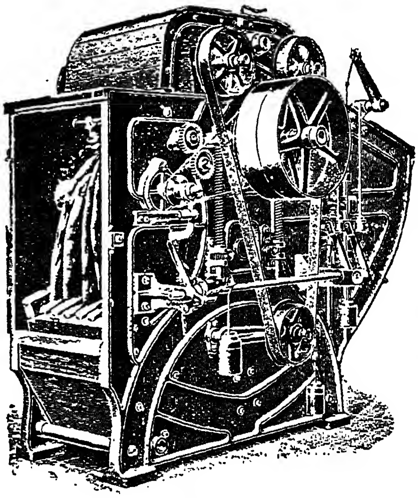

FIG. 504.

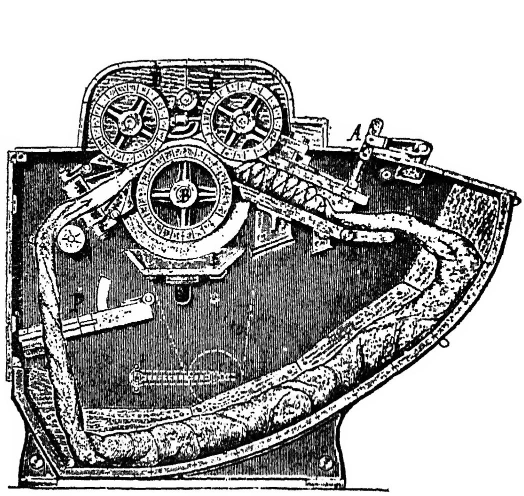

FIG. 505.

of rolls, *A*, *B*, and *C*, which press the pieces in their passage from one vessel to the next, while a slow current of water enters at *R* and takes a zigzag course through the succeeding vessels; a little soap and soda solution is gradually added in vessels 1, 2, and 3, which are heated by steam-pipes, while the dirty water is discharged continuously from *S*.

For making certain articles, woollens must be subjected to Milling, which transforms them into more or less close cloth.

When the pieces are rolled up, moistened with soap solution, and then continually compressed and rubbed together, the wool is felted and cloth formed in the course of a few hours. The milling machine in which this is effected is shown in Figs. 504 and 505. The material is caught between the three wooden rollers, *A*, *B*, and *C*, which compress them and force them into the wooden channel, *R S*, where the pressure of the plate, *R*, may be increased by the spring, *A*; the expressed liquid collects in the channel, *E*, and is at first returned but later discharged. If any knots were formed they would stick at *P* and raise a spring, *T*, thus stopping the driving-belt. With certain heavy fabrics already soaked with oleine, milling is carried out with addition of a little soda solution, which saponifies the oleic acid. In some cases dilute sulphuric acid is used, but better results are apparently obtained with 1 per cent. lactic acid solution, the wool then retaining greater lustre and elasticity (G. Ita, Ger. Pat. 236,153 of 1910).

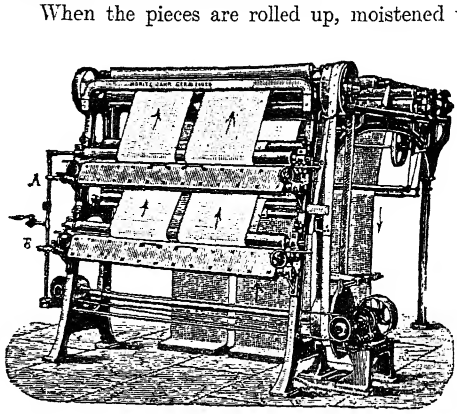

FIG. 506.

Some fabrics which are required to take bright designs and a very smooth and shiny surface (*satin*, etc.) are freed from the down always accompanying textile fibres—especially after washing, etc.—by passing them, quite taut, quickly over a row of gas-jets (or over a sheet of heated copper or a strip of metal heated electrically) which burn the hair on the

face and sometimes on the reverse of the fabric too (*see* Fig. 506, where the gas-jets run horizontally from A and B).

The removal of cotton fibres or bits of vegetable matter (which would become more

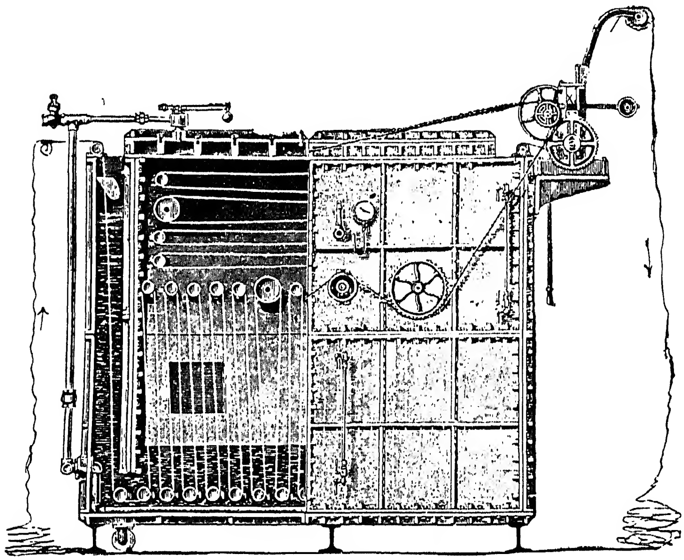

FIG. 507.

noticeable after dyeing) from woollens may be effected by hand, but is more commonly attained by **Carbonisation.** In this the fabric is impregnated uniformly with sulphuric acid of about 4° Bé. (or aluminium chloride solution), centrifuged and heated at 125° to 135°

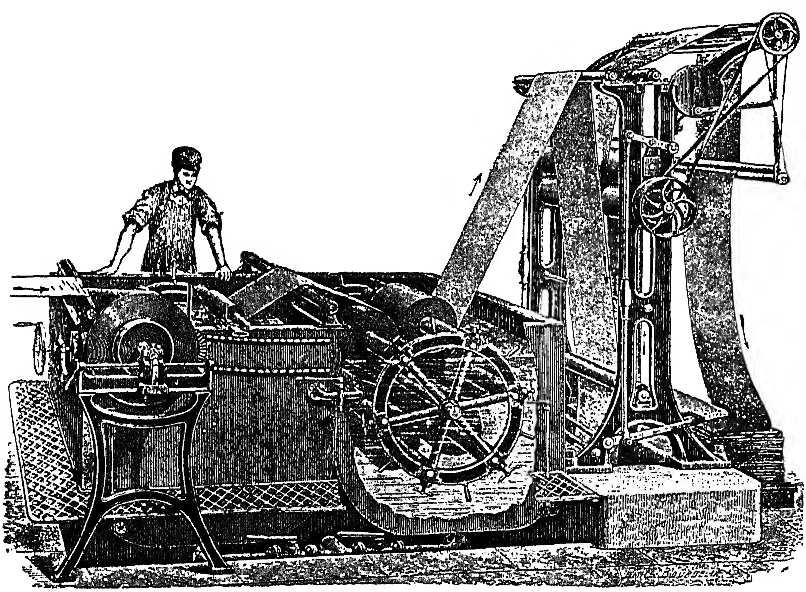

FIG. 508.

—being passed at width either over a series of tinned sheet-iron or copper rollers (similar to those used for drying woven goods after dyeing) through which steam at 2 to 3 atmos. is passed (*see* Fig. 531, p. 848) or else slowly through a large oven heated with hot air or with branched pipes fed with steam under pressure (*see* Fig. 507). In this way all the

vegetable fibres are incinerated or carbonised and are eliminated in the subsequent souring, which occupies an hour and is effected by means of a large quantity of water in the washing vessels already described (Figs. 499, 500).

As has been mentioned, woollen fabrics exhibit a tendency to felt and shrink, and these

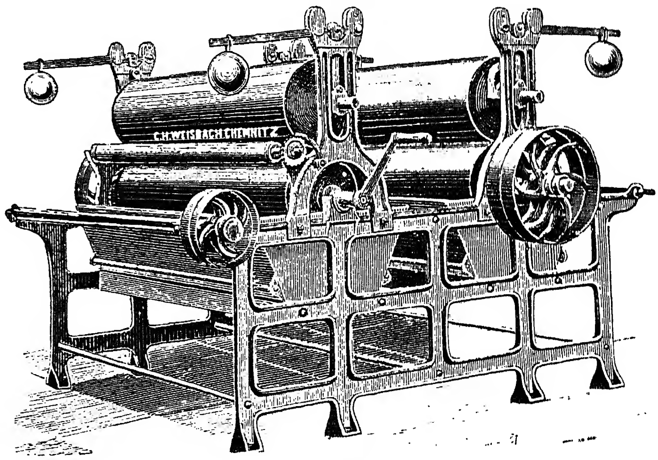

FIG. 509.

actions may become very pronounced during dyeing, when the material is kept moving in boiling baths for two or three hours. In order to avoid these changes, which likewise often spoil the design, the fabric is subjected to fixing, which consists in heating it in a *stretched* condition in vigorously boiling water, *i.e.*, at a temperature rather higher than any it will experience in subsequent operations; scalding of the fibres in this way causes

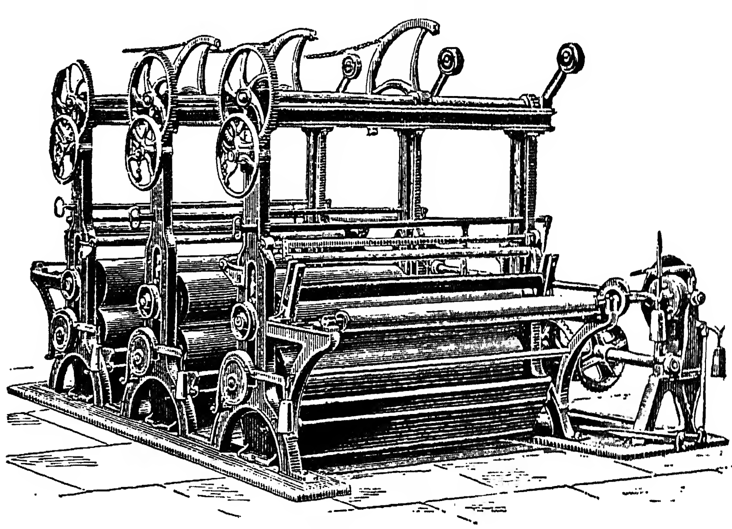

FIG. 510.

partial loss of their elasticity and power of contraction, and the fabric shrinks less during dyeing. Light fabrics are fixed in the so-called revolver machine (Fig. 508), in which the material is wound in compact rolls on reels dipping into a vessel of water kept briskly boiling; each reel may have six rolls and one reel is arranged in each of two adjacent vessels. The axis of each reel revolves during the winding, and when the first reel has received the first six rolls, the first roll begins to unwind to form another on the second reel, so that the part of the fabric which was peripheral on the first roll becomes central in the roll of the second reel. This procedure prevents any subsequent irregularity of colouring

owing to the more ready and more intense fixation of the dye on the parts subjected to the most prolonged action of the boiling water. Each roll may contain from 100 to 300 metres of fabric, which is fixed in about an hour.

Certain heavy woollens with a satin surface (and also mixed wool and cotton goods—*unions*—or cotton goods with a satin foundation) are fixed, and at the same time furnished with a lustre which persists even after dyeing, by so-called *crabbing*. The machine in which this is carried out consists essentially of two or three pairs of superposed heavy rolls of solid iron (Figs. 509, 510). One-half of the lower roll of each pair dips into a long narrow vessel of water kept boiling by direct steam. The stretched, smooth cloth is wound in compact rolls on the lower roll, and is then allowed to revolve for 30 to 40 minutes in the boiling water, being pressed by the upper roll, which revolves freely and can be weighted by means of levers. The fabric then passes to the lower roller of the adjacent vessel and so on.

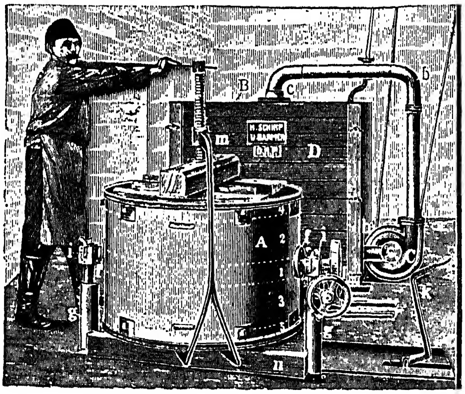

FIG. 511.

DYEING. Cotton and wool in flock were at one time dyed by immersing them—in cloth or net—in open wooden vessels containing the hot dye-bath. Use was afterwards made of mechanical apparatus similar to that shown in Fig. 495, where the material remains stationary on a false bottom, below which the liquid is drawn off and pumped to the top.

It was, however, often found that the liquid did not pass uniformly through the whole of the fibre but went more easily through that which was least compressed and which contained channels, thus producing irregular dyeing. Almost universal use is now made of mechanical apparatus similar to the above, but with the fibre highly compressed (*see* Fig 511). In this case the pump, which must be more powerful, causes complete penetration of the liquid, and much better results are obtained. Skeins of yarn can also be dyed in this apparatus when they are well compressed. After the discharge of the dye-bath (kept, if required, for a subsequent operation), the dyed fibre may be washed in the same vessel.

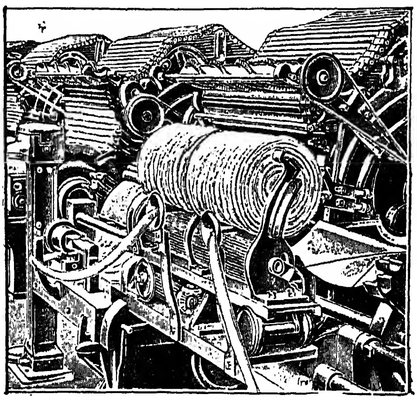

FIG. 512.

To dye combed wool (*tops*) wound on to bobbins by suitable machines (Fig. 512), very general use is made of Obermaier mechanical apparatus of the revolver type, in which the bobbins are arranged in as many horizontal, cylindrical cases fitting into a vertical cylinder closed at the top and communicating below with the pipe of a pump, which it fits exactly (Fig. 513); the mode of action is shown clearly by the figure. A more simple apparatus which carries larger charges and is largely used also for yarn on bobbins with crossed thread, is that of Halle shown in Fig. 514, where may be seen the false bottom supporting the bobbins, the pump for circulating the dye solution and the perforated cover pressed down by vertical screws. In these mechanical apparatus it is always possible to reverse the sense in which the liquid circulates, homogeneous dyeing being thus more easily obtained.

With skeins of spun fibre, various methods of dyeing are in use: in the old method, still largely used, the skeins are threaded on smooth round sticks so that one-half of the skein is immersed in the dye-bath, the skeins being turned or inverted on the stick from time to time by hand (*see* Fig. 515). The form of the wooden vessel is now simpler, as is seen

from Figs. 516 and 517, showing the perforated false bottom below which are the direct or indirect steam-pipes for heating the bath, and the perforated wall, P, outside of which the colour is gradually added so that it may not come into immediate contact with the neighbouring skeins.

A mechanical apparatus for dyeing skeins is shown in Fig. 518. The skeins are threaded

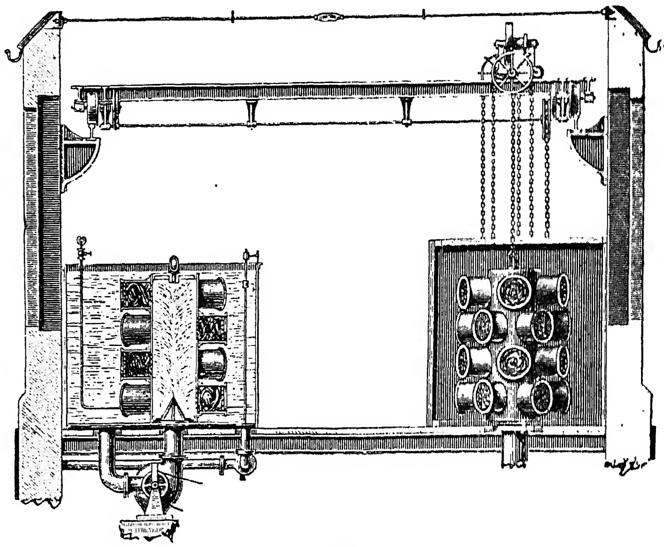

FIG. 513.

on rods which are rotated by toothed wheels, while the whole frame can be raised from or lowered into the bath by a toothed rack. Still better is the Klauder-Weldon revolving apparatus shown in Figs. 519 and 520: on a large bronze wheel, one-half of which dips into a trough while the other half is covered, are fixed axial and peripheral rods, which keep the skeins taut. The wheel revolves slowly in the dye-bath, and the pegs, b, at the ends

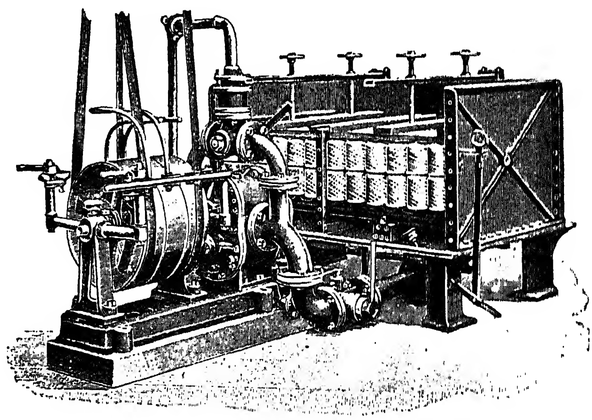

FIG. 514.

of the peripheral rods knock against an iron striker inside the trough, so that the rods revolve slightly each time; hence the skeins threaded on them are moved a few centimetres. Two workmen suffice for the charging and discharging of 100 to 200 kilos of wool or cotton, while during the dyeing one man can look after three or four of these machines, adding the necessary colour now and then by means of the copper funnel A.

The steam for heating the bath reaches the bottom of the trough by the tube d. At e is an automatic indicator which shows when any particular peripheral rod does not turn

owing to the skein being caught. The rapidity of revolution may be altered, but, as a rule, the movement is slow in order that the wool may not be felted.

In recent years a happy solution has been found to the problem of dyeing cotton or woollen yarn while still wound on the tubes of the spinning machine as spools or *cops*, thus avoiding the winding into skeins and preserving the fibre better. At first the perforated tubes of the bobbins were inserted in drums which rotated in the bath and from the interior of which the air or liquid was pumped, the bath being hence circulated from the interior to the exterior of every bobbin and *vice versa* (Figs. 521, 522). There are various other arrangements, but recently a good reception has been everywhere accorded to an apparatus devised by De Keukelaeres of Brussels. This compresses the skeins or bobbins in a square iron or copper case on to a perforated false bottom, while, before the case is covered with a perforated metal plate, the yarn is covered with sea-sand, which is forced into all the pores of the mass not occupied by fibre by means of a water-jet. The cover is then fitted and screwed tight, and the bath circulated through the mass of yarn by means of a pump capable of developing considerable pressure; the liquid may circulate from bottom to top and *vice*

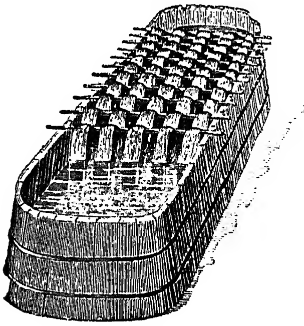

FIG. 515.

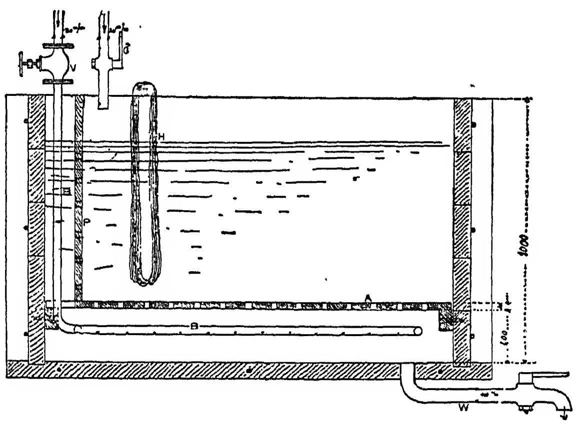

FIG. 516.

versa and, finding no channels open, is obliged to traverse the fibre uniformly. When the dyeing is finished, it suffices to place the bobbins in a perforated basket and to shake this in a vessel of water to separate the whole of the sand, which collects at the bottom of the vessel and can be used again.

For dyeing skeins of cotton with Turkey red, which is the fastest red for cotton, the latter must be prepared and mordanted. It is not bleached with chlorine but is boiled with a caustic soda solution (0·75° Bé.) under pressure (2 atmos.) for 4 to 5 hours. When washed, the skeins of cotton are passed repeatedly into a bath of neutralised ammonium sulphoricinate (20 kilos of 50 per cent. strength per 100 litres of water; *see* p. 390); this operation is readily done with a suitable machine (Fig. 523), which is fitted with ingenious contrivances for pressing, wringing, untwisting, and immersing the skeins in the sulphoricinate bath repeatedly and automatically. When thoroughly soaked, the skeins are dried at 50° to 60°, then steamed under an excess pressure of 0·5 atmos. in an autoclave for an hour, and afterwards passed into the mordanting bath, consisting of a

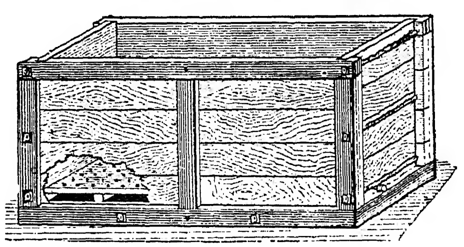

FIG. 517.

basic aluminium sulphate solution (7° Bé.) at 45° (with an iron mordant, a violet colour is obtained instead of red ; with one of tin an orange colour, and with one of chromium a reddish brown colour ; but these mordants are rarely used in practice) ; they are subsequently dried at 45°.

Use is often made next of a tepid bath consisting either of a little chalk suspended in

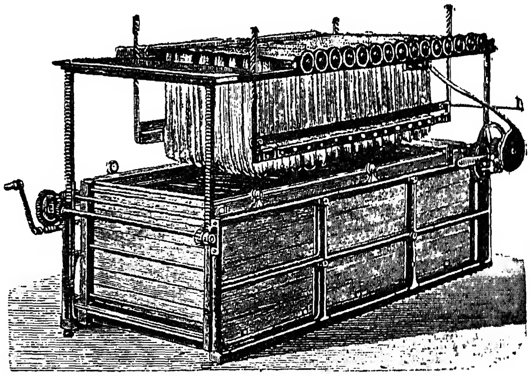

FIG. 518.

water or of sodium arsenate, to remove any sulphoricinate not stably fixed, and hence to give subsequently a brighter colour. After this preparation, the skeins are passed into the dye-bath (10 to 15 per cent. of alizarin paste, calculated on the weight of cotton) contained in wooden vats and heated by tinned copper steam-coils ; the temperature is first kept at 25° for an hour and is then raised in 30 minutes to 65° to 70°, the goods being manipulated for an hour. The dyed skeins are dried and are often introduced, without washing, into a

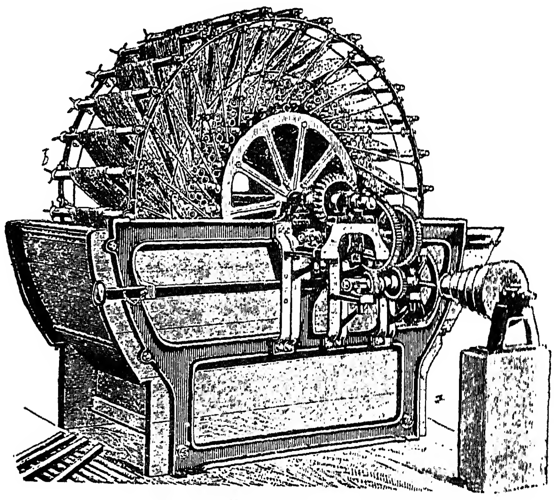

FIG. 519.

second sulphoricinate bath, being then steamed for an hour in an autoclave at 1 atmos. ; the colour is not very bright but is made so by immersing the material for half an hour in a 0·5 per cent. soap solution heated under slight pressure (0·5 to 0·25 atmos.). Thorough washing with water is followed by drying at a gentle heat. Although Turkey red is removed to a small extent if the material is scoured with a white fabric, yet it is the fastest red against washing and light now prepared on cotton. Kornfeld (1910) regards the fastness of Turkey red as due, not to the constitution of alizarin, but rather to the formation of a highly resistant double salt of aluminium oleate and the calcium salt of alizarin, and still more to the polymerisation of the fatty acid molecules under the action of steam.

According to a patent by Kornfeld, Turkey red dyeing may be carried out in the usual

mechanical apparatus with circulation of the bath, the alizarin being rendered soluble by means of sucrate of lime.

Cotton Fabrics are sometimes dyed in ropes with vessels similar to those used for wool (*see later*), but more usually in the so-called *jigger* (Fig. 524), which is a rather shallow wooden trough provided with two outside rollers worked alternately by gearing so as to wind or unwind the pieces (3–4); the latter are sewn end to end and are kept quite taut,

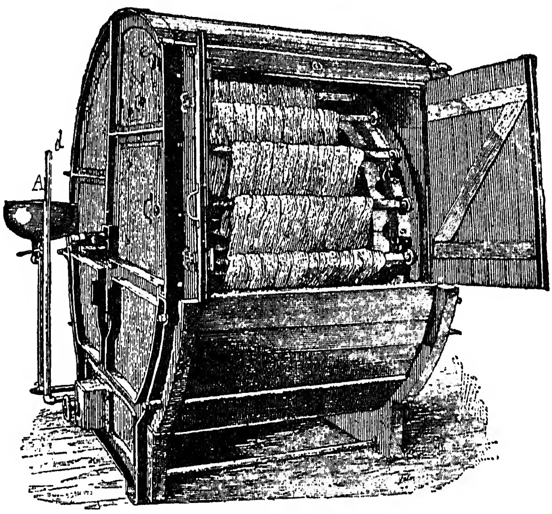

Fig. 520.

and pass below two small rollers close to the bottom of the trough. The dye solution in the bath may be heated at will by direct or indirect steam.

The jigger is often used also for dyeing *unions*, *i.e.*, fabrics composed of cotton warp and wool weft, since these do not cockle or wrinkle, as all-wool goods would do, when passed under tension from one roll to another.

Woollens are usually dyed in wooden vessels provided with one or two reels which raise the goods in ropes from the front part of the vessel and drop them into the bath,

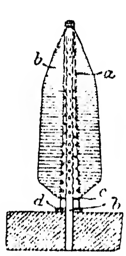

Fig. 521.

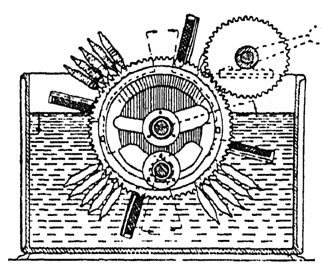

Fig. 522.

the inclined wall at the back forcing them in folds on to the bottom of the vessel itself (Figs. 525, 526).

In some cases the velocity of rotation of the reels can be varied at will, being accelerated at the moment when the colour is introduced into the perforated compartment which admits of its gradual passage into the whole of the bath. The perforated steam-pipe also passes into the bottom of this compartment and is so arranged that the steam does not strike against the pieces, as this would result in irregular dyeing. The velocity of the reel must not be too high (20 to 50 cm. per second), as otherwise the wool would felt and the bath cool too rapidly. When the pieces are introduced into the vessel, one end is thrown over the reel and then stitched with twine to the other end (*see* Fig. 526). In some cases the materials (*e.g.*, cashmeres) are twisted, by the movement in the trough, into very thin

cords, into which penetration of the colouring-matter is difficult and irregular; in order to avoid these disadvantages, such fabrics are first folded in two lengthwise and the selvedges then stitched together.

During the dyeing operation, the dyer cuts off small samples of the fabric from time to time, washes them, dries them in a warm towel and compares them with a specimen, so that fresh addition of colour may be made where necessary. Such fresh colour is dissolved

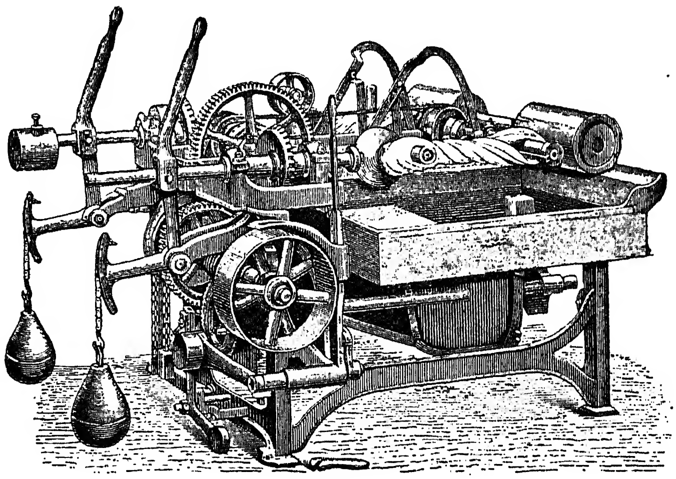

FIG. 523.

apart in a wooden bucket in a few litres of the hot dye-bath, the solution being always passed through a very fine hair-sieve to remove granules of undissolved dye, which would spot the material; the steam-cock is closed while the new dye is being gradually added.

The dyeing of woollen fabrics is commenced with a bath of tepid water (40° to 50°) with the addition of 10 to 15 per cent. of crystallised sodium sulphate and 2·3 per cent. of concentrated H_2SO_4 (or 5 to 6 per cent. of sodium bisulphate) (these proportions referring to the weight of the fibre). The colouring-matter (a few grams for pale colours and as much

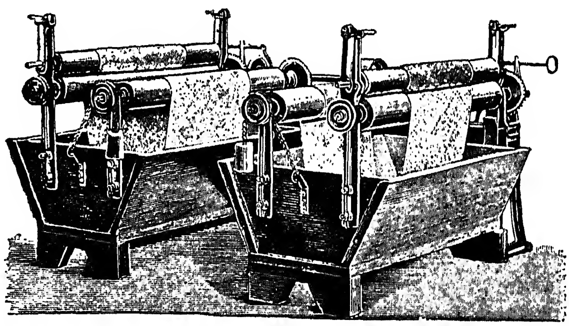

FIG. 524.

as 5 kilos of black per 100 kilos of material) is added in several portions at the beginning of the operation, the goods being slowly moved meanwhile. In the course of an hour the bath is brought to boiling and this may last one or two hours before the dyeing is complete. Finally the steam-tap is shut and the goods discharged into a vessel of cold water.

After being rinsed and folded roughly by hand they are left to drip on beams for some time, a further part of their water being removed by two or three minutes' centrifuging (*see* p. 565). The goods are then ready to be dried in the apparatus described later.

When very delicate wool or wool and silk fabrics (with gathers and embroidery) are to be dyed, they are sometimes wound concentrically on hooks fitted to a frame such as

that shown in Fig. 527. In this case the frame is only moved now and then, so that the fabric may not be injured.

Textile Fibres in Flock are dried in a series of superposed chambers with perforated bases on which the moist, centrifuged fibre is spread (Fig. 528, I.). At II. is seen a counterpoised elevator on which is placed the charged chamber ready to be introduced into its position in the series in place of one containing fibre already dried. The

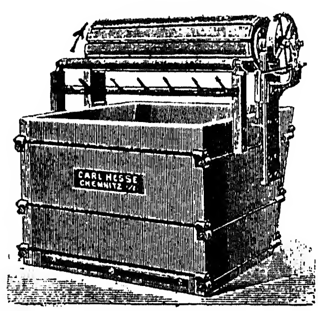

FIG. 525.

drying is forced in by the fan, *A*, a
chambers are dried first, and whe
automatically and fresh ones intro
be dried in these chambers.

Skeins of yarn may be dried b
these horizontally in frames in a
the moist air issues from vent-hol

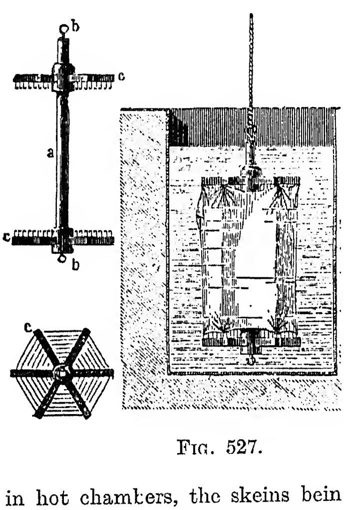

FIG. 527.

in hot chambers, the skeins bein
steam-pipes, as is shown in Fig. 5
Good results are also obtained
are placed on rods, etc., carried b
at *A* with hot, dry air. The dry
an outlet at *B*.

Fabrics as they come from t
stretched, over a battery of seven
regularly by gearing, the rate be
actuated at a point more or less
latter is turned by the pulley *A*,
mission.

The dried fabrics are then exa

a well-lighted window in order to ascertain if there are any defects in dyeing or otherwise, so that these may be remedied before dressing.

Dressing of Fabrics is effected by impregnating them with solution of gum, bone glue, starch, etc. The fabric is passed beneath a roller dipping into a vessel containing the solution, and is then pressed by a second roller superposed to the first in a kind of *foulard* like that shown in Fig. 532; the vessel may have the section shown in Fig. 533. The gummed fabrics are subjected to mechanical treatment varying according to the type required. Dressing

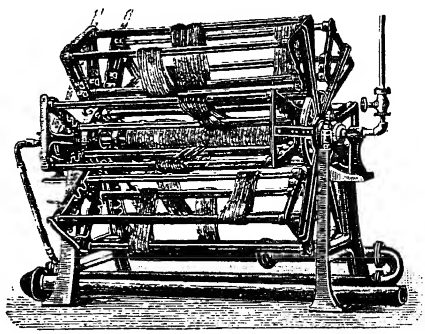

FIG. 529.

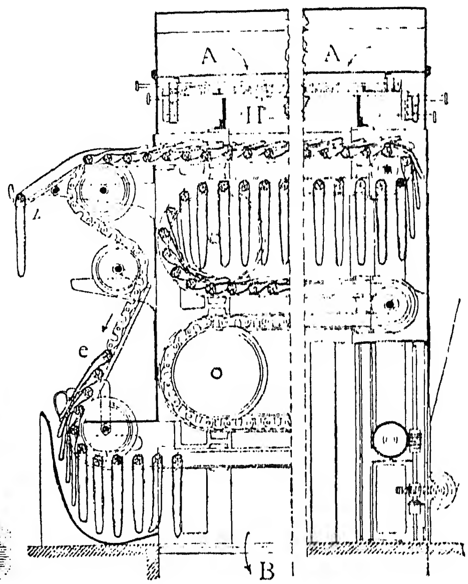

FIG. 530.

increases the strength and weight of the tissue, which is next dried and at the same time pulled out both lengthwise and breadthwise in order to bring it back as nearly as possible to the dimensions it possessed before dyeing. This is effected by means of the so-called *tentering frame*, into which the tissue passes, fixed laterally by the selvedges on two

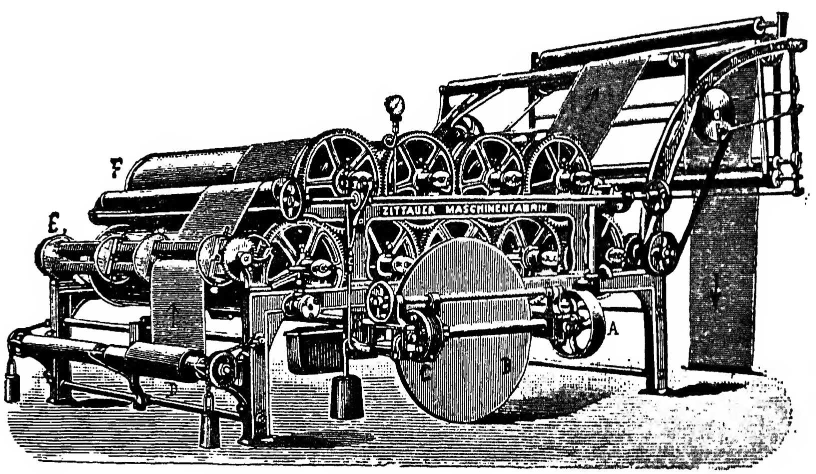

FIG. 531.

chains carrying clips or needle-points; the distance between the two chains is gradually increased to the desired width, which is shown on a graduated iron bar, *A* (Fig. 534). Fig. 535 shows a complete frame with the gumming machine, *B*, and two operatives fixing the selvedges on the points of the chains. The widened cloth is dried throughout its whole length by a current of hot air blown into a long chamber beneath, and finally by a heated drum, *C*. These frames are 8 to 12 metres long, but are sometimes constructed

on several stories in order to save length. Fig. 536 gives a better view of the frame in outline: the gummed, centrifuged, and folded cloth lies ready on the two benches, *B*; the air is heated at *T* and the fan, *V*, forces the hot air into the long chamber, *R*; the cloth enters at *B* and issues at *C*.

Milled fabrics and certain others which are required to present a hairy surface are

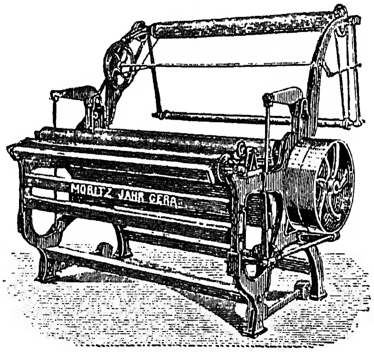

FIG. 532.

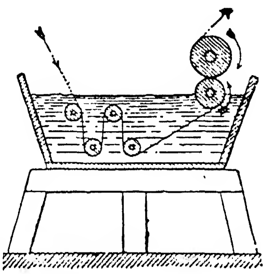

FIG. 533.

passed to the so-called *raising gigs* (Fig. 537), consisting of one or more large drums carrying numbers of metallic points or strings of the spiny capsular heads of *Dipsacus fullonum* (10 to 20 cm. in length, Fig. 538) on spindles. The drums or spindles revolve so that the points just touch the stretched surface of the cloth and draw from it fairly long hairs, which are then rendered uniform by passing the dry cloth to the cutting and brushing machines furnished with cylindrical brushes and with drums fitted with cutting edges arranged helically (*see* Fig. 539); the first brush, *A*, raises the hair, the cutter, *B*, cuts or crops it off uniformly, and the second brush, *C*, sets it regularly all in the same direction.

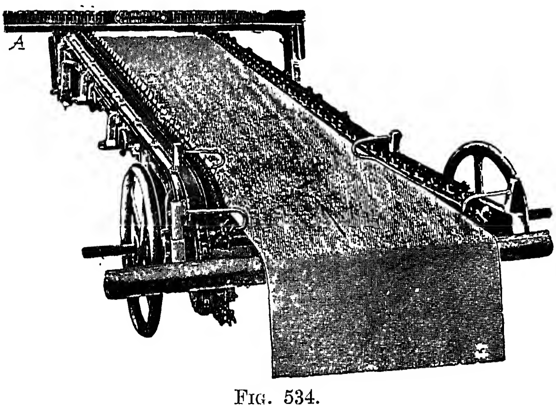

FIG. 534.

A similar operation is carried out with velvets, which are, however, woven specially, and often in two superposed pieces attached by a large number of fibres, which are then cut exactly in two so as to give two separate pieces each with a hairy face.

When the fabrics are required to have a very smooth, shiny surface, they are passed after gumming to the so-called *calenders*. A common type of the latter for wool and unions, which require but little pressure, is that shown in Fig. 540: the cloth is seized by the selvedges by two discs fitted with bands, *A* (called a palmer), which enlarge the cloth to the required size and then pass it on to a continuous felt, *C*, which transfers it in a well-stretched and compressed condition on to a copper drum, *B*, heated by steam under slight pressure. For cotton or cotton and silk fabrics, use is made of calenders with several superposed and heated cylinders to which pressure may be imparted by means of suitable levers (Fig. 541) in such a way as to exert a kind of friction on the cloth passing from one

cylinder to the other. When a very high finish is required on certain *satin* fabrics of cotton, they are passed between two massive steel cylinders which are under very high pressure (hydraulic) and one of which is fluted with very fine striations (as many as 10 to 25 per

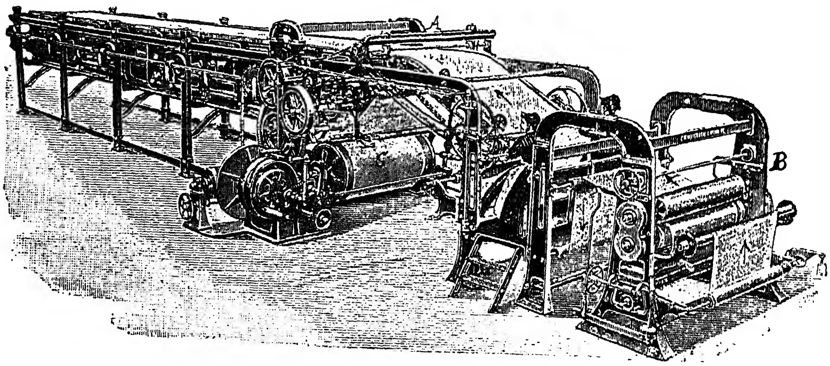

FIG. 535.

millimetre, as suggested by Schreiner); these leave their stable imprint on the fabric like so many minute, shining cylinders like silk fibres, which reflect light under any angle; this finish is known as *silk finish* (or Schreiner finish). Similar calenders are used for obtaining special watered effects (*moiré*).

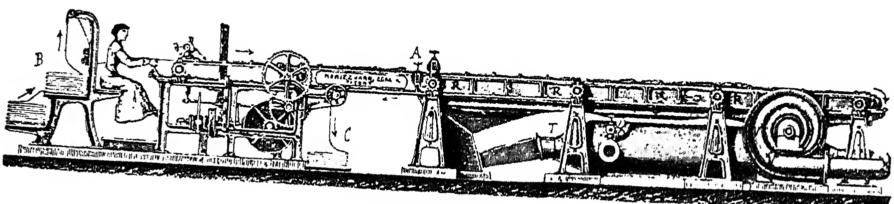

FIG. 536.

On woollen fabrics calenders generally produce a so-called false finish like that of a bright sheet of metal. This is not regarded as desirable by the merchants, and, further, such a finish will show rain-drops, even after drying. In order to avoid this inconvenience and the better to fix the material in both directions, so that it will not shrink when worn,

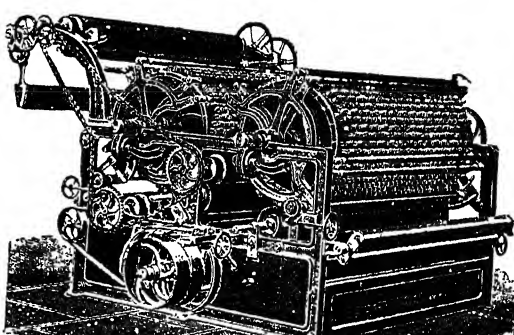

FIG. 537.

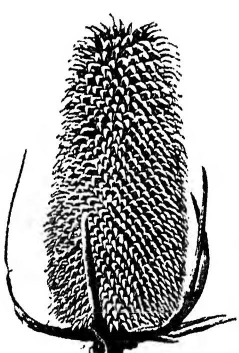

FIG. 538.

it is subjected to so-called *steaming*, *i.e.*, to the action of steam under a pressure of 2 to 3 atmos. (some colours will not withstand this operation). The fabric is well stretched and wound, together with a cloth, round a perforated cylinder; the roll of two or three pieces thus obtained is wrapped in cloth fastened by strings, the cylinder being then fixed vertically on a steam-cock (Fig. 542). The steam, under pressure, is obliged to traverse the

whole of the roll of fabric, and when it issues in a dense cloud (after a few minutes) the operation is at an end; the roll is then removed, but is allowed to cool without unrolling, since in that way it acquires a better and more resistant lustre. The latter is also found to

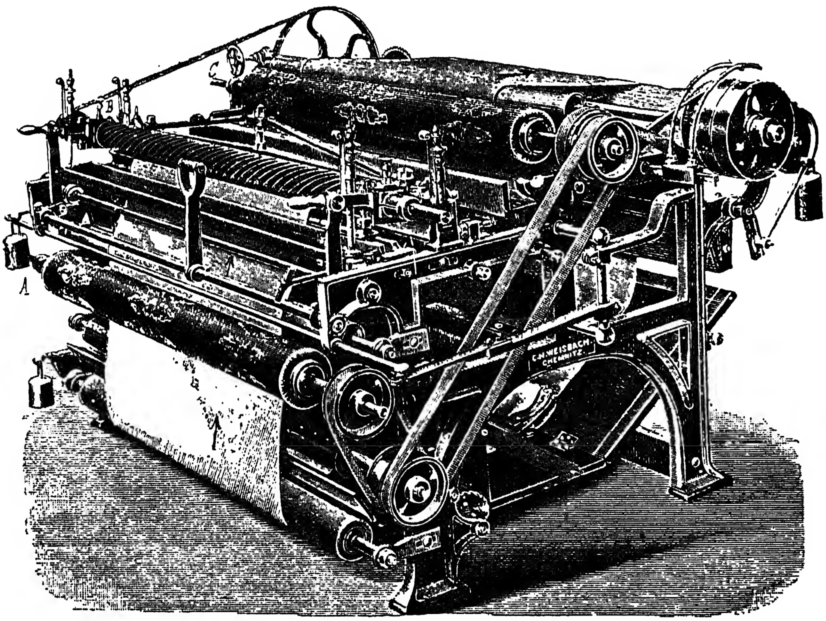

FIG. 539.

be improved by carrying out the steaming in a vacuum, the rolls G H (Fig. 543) being introduced into a kind of horizontal jacketed autoclave, X, previously heated by passing steam through the jacket; when the cover L has been tightly closed, the autoclave is evacuated by passing steam into it and condensing the steam by a water-spray in the cylindrical chamber, W, which communicates with the autoclave by means of the tap, R. After this

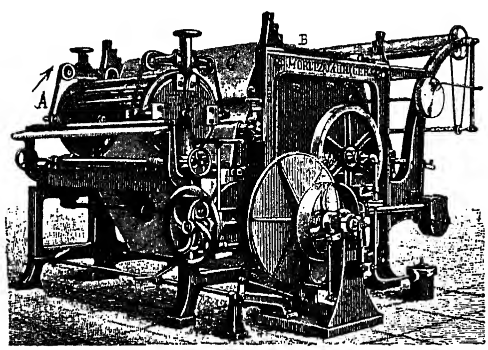

FIG. 540.

the steam is passed through the roll of fabric, either from the inside to the outside or *vice versa*, by fixing the roll in a suitable manner to the steam-cock.

Of the various other operations comprised in the finishing of fabrics, only that of *pressing between hot card* need be referred to; this gives lustre to cloths which are not subjected to steaming and in general imparts a very soft, pleasant feel, more particularly to the finer woollens.

In this operation, which is the last of importance, the best effect is obtained when

10 to 15 per cent. of moisture is present, so that fabrics which are too dry are treated first with a slight steam-jet, being meanwhile wrapped on drums in large rolls.; after some

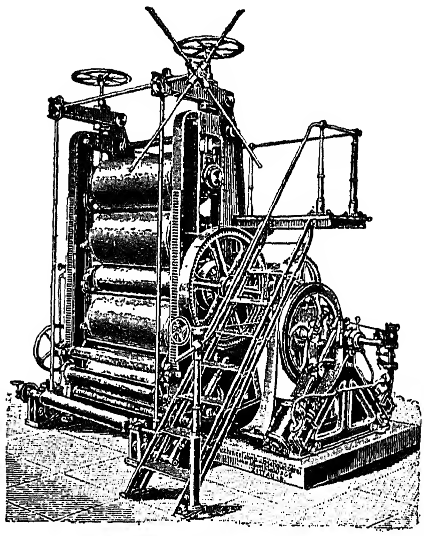

FIG. 541.

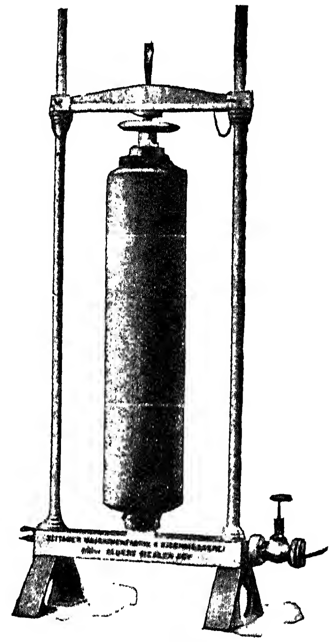

FIG. 542.

hours these rolls are unwound and the fabric arranged in regular folds, between each adjacent pair of which is inserted a piece of hot, smooth card. The whole is then left under pressure in a hydraulic press (Fig. 544) for 10 to 12 hours. In order to obtain uniform

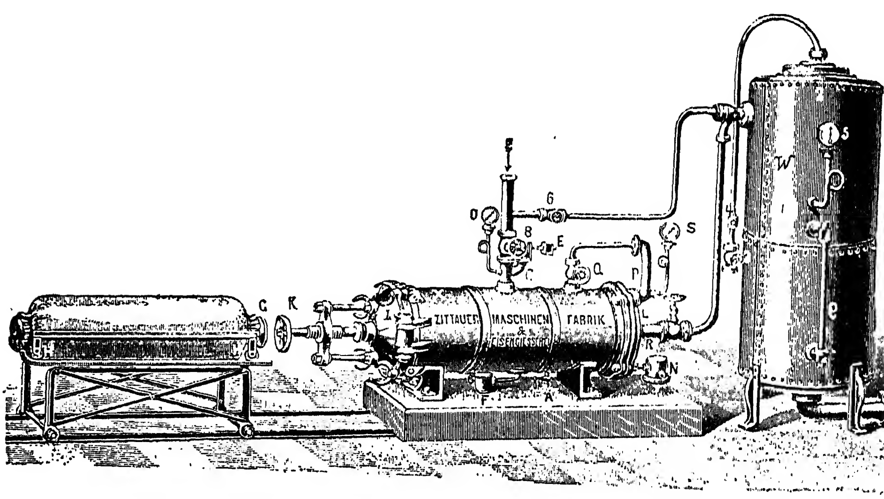

FIG. 543.

heating while the pressure is being exerted, presses are now used with double pillars in which steam circulates (Fig. 545); also the pillars are sometimes heated electrically.

For the folding or rolling of fabrics, and also for measuring, simple and rapid machines have been devised.

For the Mercerisation of cotton yarn in hanks (*see* p. 808) a machine such as that shown

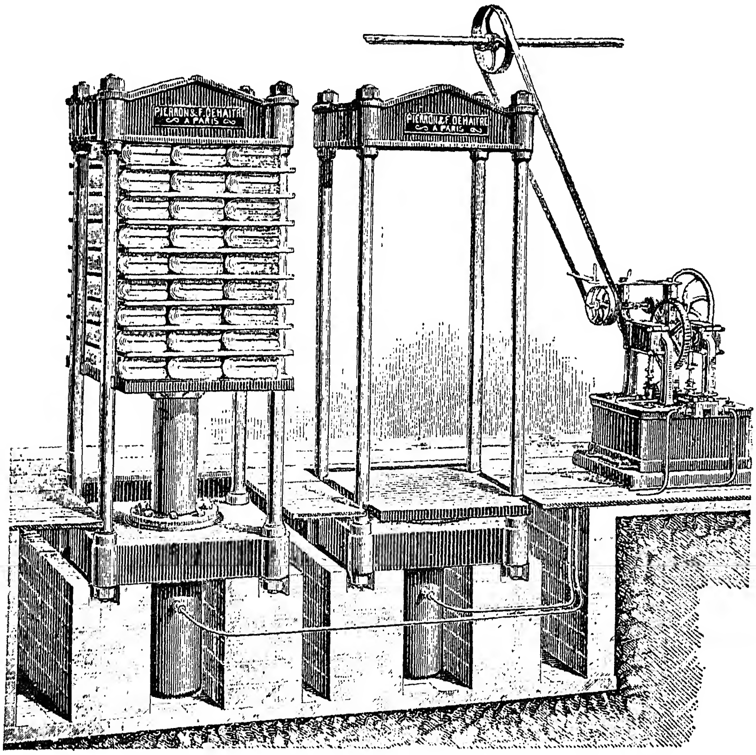

FIG. 544.

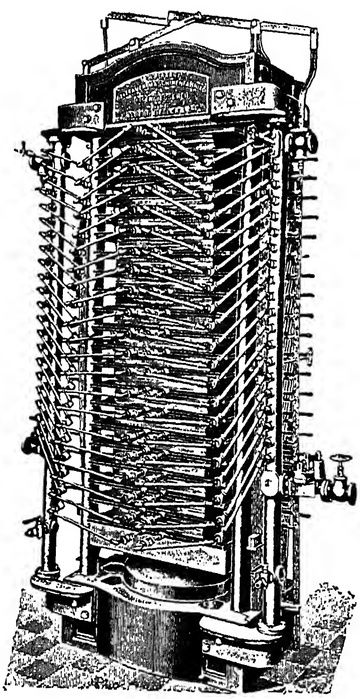

FIG. 545.

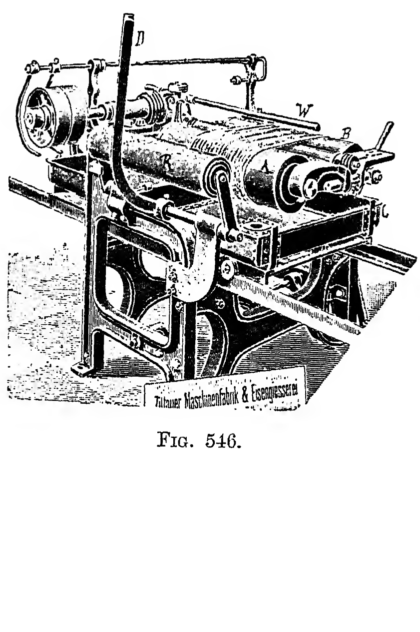

FIG. 546.

in Fig. 546 is used. The uniformly moist skeins, as they come from the centrifuge, are stretched in a thin layer between the two cylinders, *A* and *B*, the distance between which can be increased so that the skeins are considerably stretched. Then, when the rollers are revolving, a lever is operated to raise the iron vessel, *C*, containing cold caustic soda solution of 25° to 30° Bé., one-half of each cylinder dipping into the soda. At the end of a few minutes the imbibition is complete, the soda solution is drawn off into a tank provided with a pump, while a copious supply of water is sprayed on to the skeins, which are pressed by the roller, *R*. When washing is complete, the tension is relieved and the skein removed.

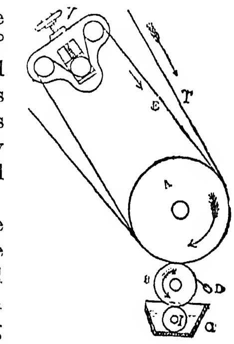

FIG. 547.

There are also other machines for mercerising fabrics, these being kept stretched by contrivances similar to those used in the tentering frame (*see* Fig. 534), while the caustic soda is removed from the fabrics by means of suction pumps. The fabric is then washed with a little hot water so as to give a moderately strong solution of caustic soda, which may be used to dissolve solid caustic soda or may with advantage be concentrated in multiple effet evaporators (*see* Vol. I., p. 567). The caustic soda is removed completely from the fabric by thorough washing in cold water, then in a slightly acid bath and finally in water.

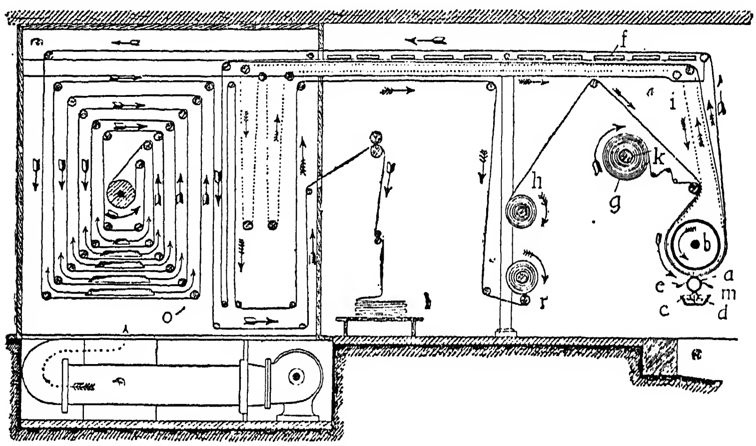

FIG. 548.

The Printing of textiles, as indicated on p. 831, is carried out by pressing, with a rubber roller, *A* (Fig. 547), the fabric or yarn against a copper cylinder, *B*, on which the design is engraved. The copper cylinder receives the pasty colour from a roller, *I*, dipping into the vessel, *C*, containing the thickened colour solution, a blade, *D*, then scraping away the excess of colour so that only the hollows of the design remained filled. Between the rubber cylinder and the fabric, *T*, to be printed runs a continuous band, *E*, which is kept taut by the contrivance, *V*. The arrangement used, with the adjacent drying chamber, *o*, is shown in Fig. 548: the vessel of colouring-matter is at *cd*, and the fabric is unwound from *g* together with the accompanying cloth *h*, and the continuous pressure cloth *i*; the dyed and dry fabric is collected in folds at *l*, while the cloth *h* is rewound at *r*, and *i* returns constantly to the printing cylinder. When several colours are to be printed on one and the same fabric, a number of rolls and colour vessels are required, as is shown diagrammatically in Fig. 549.

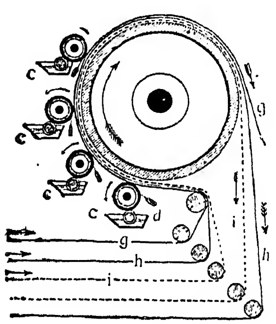

FIG. 549.

Fig. 550 shows a complex machine for the printing of textiles in twelve colours at once; highly skilled workmen are required to regulate its working with accuracy.

A simple arrangement for printing yarn in skeins by hand is shown in Fig. 551. The skeins are kept taut between the rods *A* and *B*, and the printing rollers, which are not very clear in the figure, are below *A*. The printed skeins are hung on rods fitted to a framework, this being introduced into an autoclave to be treated with steam under pressure (Fig. 552).

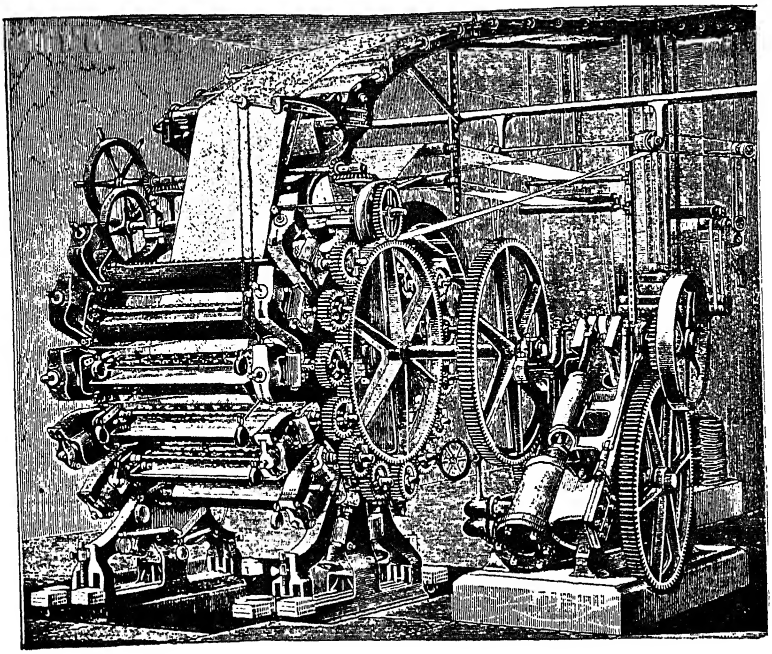

Fig. 550.

Printing colours are boiled with the thickening agents in suitable double-bottomed boilers, heated by means of steam and furnished with stirrers. Fig. 553 shows a battery of such colour-pans.

When mention was made of *aniline black* (p. 768), it was stated that the complete

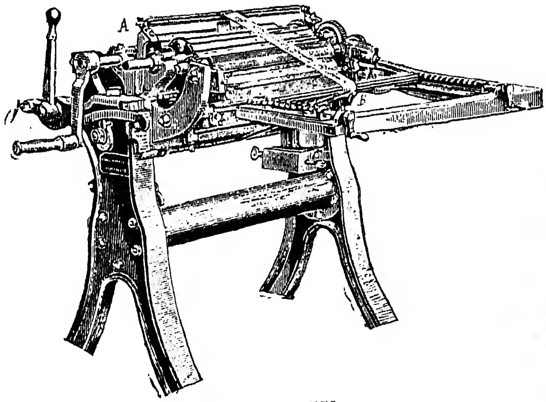

Fig. 551.

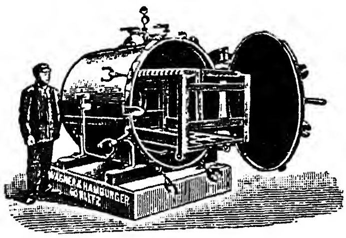

Fig. 552.

development of this colour is obtained in an oxidation chamber (Fig. 554). In the case of yarn, the method of continuous drying illustrated in Fig. 530 gives good results, but with fabrics use is generally made of a chamber with revolving rollers, where the fabric traverses slowly a very long path and issues completely black; a hood is arranged to carry off acid vapours. Of great importance in this operation is the regulation of the temperature of

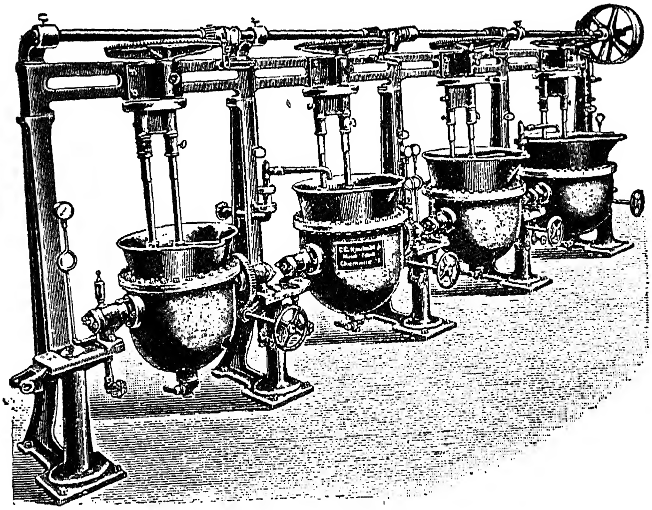

FIG. 553.

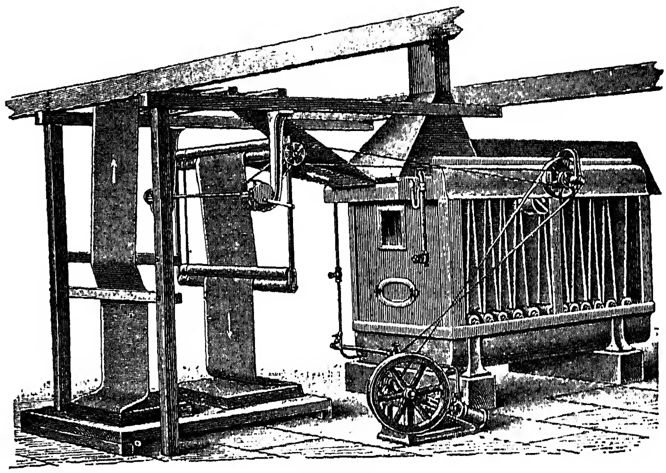

FIG. 554.

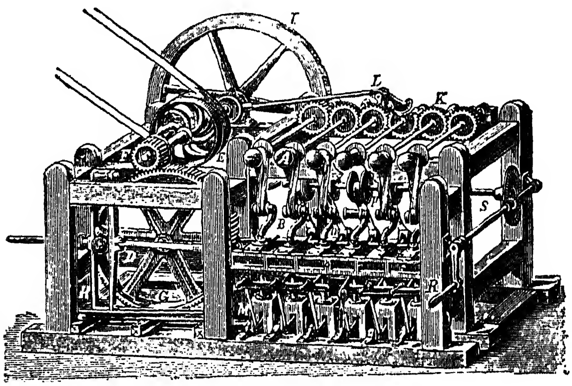

FIG. 555.

the draught and of the velocity with which the fabric passes through the chamber. Unexpected stoppages are dangerous, as they may lead to corrosion of the fabric or alteration of the colour.

To *polish* and *soften* silk, the skeins are stretched, twisted, and rubbed repeatedly on a smooth rod fixed in the wall. But nowadays this is done by machines (Fig. 555), which act automatically and give a large output.

DD. PROTEINS OR ALBUMINOIDS

These are fundamental products in the formation and constitution of animal and vegetable organisms. The protoplasm of vegetable and animal cells, which is the origin of the metabolic processes and hence of the life of the organism, consists of protein substances, which are also indispensable components of foodstuffs.

From a physiological point of view they are therefore of the utmost significance, but their chemical nature is very complex and is still little understood, although the investigations of Emil Fischer and a number of able collaborators during the past thirty years have to some extent pierced the veil surrounding this most important group of organic compounds, which had been previously studied, as regards some of their more superficial characters, by Ritthausen, Hoppe-Seyler, Hammarsten, Neumeister, Pflüger, Hedin, Küster, Nencki and Sieber, etc.

The numerous substances comprised in this group are all composed of C, H, O, N, and S, with, in a few cases, P; their percentage compositions vary between the following limits: C, 50 to 55; H, 6·9 to 7·3; O, 19 to 24; N, 15 to 19; S, 0·3 to 2·4. The heat of combustion of 1 grm. of protein substances varies from about 5000 to 6000 calories.

The proteins have high refractive indices. Their solutions are lævo-rotatory, the specific rotation varying with the concentration and with the salt content; protein ions have higher rotations than the neutral proteins.

The molecular magnitudes of these substances cannot be established with certainty, since it is not easy to isolate single individuals, only very few of them crystallise, none are transformable into vapour, and in no case are true solutions obtainable capable of cryoscopic or ebullioscopic measurement; their solutions are colloidal. Direct or indirect attempts to determine their molecular weights have given numbers varying from 10,000 to 30,000.

Both the sulphur and the nitrogen occur in two groupings, being partly removed by hot potash and partly more stably combined.

Absolute alcohol coagulates proteins and precipitates them to some degree unchanged from their aqueous solutions. They are also precipitated unaltered by solutions of sodium chloride, magnesium sulphate or ammonium sulphate of different concentrations, which are characteristic of the various proteins.

Proteins are coagulated and precipitated from their aqueous solutions by small quantities of mineral acids (nitric acid may be in excess). They have a feeble acid character and form salts as insoluble precipitates with metallic salts, *e.g.*, ferric chloride, acidified mercuric chloride, copper sulphate, etc., and they dissolve small amounts of freshly precipitated ferric hydroxide. From these metallic precipitates proteins are liberated in a changed form.

Less pronounced is their basic character (like the amino-acids, they behave as both acids and bases at the same time), although egg-albumin is completely precipitated by weak acids, such as tannin, phosphotungstic acid, and picric acid.

Aqueous solutions of the proteins are coagulated on heating to different characteristic temperatures, and the coagulated proteins dissolve only in an excess of acid or alkali in the hot, their constitution being modified thereby

and H_2S and NH_3 sometimes evolved: with alkalis they form albuminates, and with acids **Aicd-Albumins** (*syntonins*, *see* p. 862), both insoluble in water and reprecipitable by neutralisation. By the protracted action of these two reagents (**Hydrolysis**, *see below*) or by the action of pancreatic juice, which contains **Tryptase** (*see* p. 134), they yield various amino- or diamino-acids: glycocoll, alanine, phenylalanine, aspartic acid, glutaminic acid, leucine (in abundance), pyrrolidinecarboxylic acids, tyrosine, serine, triaminotrihydroxydodecanoic acid, β-indoleacetic acid, arginine, lysine, ornithine, tryptophane, cystine (sulphur compound), etc., all of them optically active with the exception of glycocoll. When a piece of boiled egg-albumin is heated at 37° with gastric juice, it rapidly dissolves with formation of **Peptones** and **Albumoses.** The peptones, passing into the intestines, undergo further hydrolysis, and as final products yield amino-acids. The complete hydrolysis of the albumin may be effected more rapidly by means of a concentrated acid (*e.g.*, HCl), which gives amino-acids and also ammonia. By putrefaction various other substances are formed: **Ptomaines**, such as cadaverine (*see* p. 257), putrescine or tetramethylenediamine, etc.; glucosamine, methylamine, ammonia, β-indoleacetic acid, phenylacetic acid, carbonic acid, hydrogen sulphide, formic to caproic acids, partly of normal structure and partly optically active (valeric and caproic) etc.; indole, skatole, phenol, cresol, mercaptan, methane, etc., all of these being oxidation or reduction products of the original compounds obtained. The action of pathogenic bacteria on proteins yields poisonous substances, the **Toxalbumins**, which are similar in composition to the proteins and lose their toxicity when their aqueous solutions are heated.

The following *reactions* are characteristic of the proteins:

Protein solutions give a violet coloration (like biuret) with alkali and a few drops of 2 per cent. copper sulphate solution (*biuret reaction*).

With nitric acid in the hot and even in excess a yellow precipitate is formed (*xanthoprotein reaction*).

With Millon's reagent (*see* p. 828) a red coagulum is formed on boiling.

The degradation or *hydrolysis* of proteins, when it is complete and takes account of all the more or less complex groups composing the protein molecule, will permit of an attempt, with probability of success, to synthesise these substances completely. Such more or less gradual decompositions are attained by protracted heating (for different times with different proteins and in some cases for 200 hours) in an autoclave, or by means of soda or baryta (Schützenberger), or, better, 25 per cent. solutions of hydrochloric or sulphuric acid. Even under these conditions, however, some of the intermediate compounds cannot be detected, the hydrolysis being in many cases too rapid. Hugounenq and Morel (International Congress of Applied Chemistry, London, 1909) have obtained a somewhat more gradual hydrolysis by using 15 to 25 per cent. hydrofluoric acid solutions and heating for 100 to 150 hours. Interesting results were obtained by N. Zelinsky (1912) with formic acid (1 to 30 per cent.), best at a high temperature and pressure.

The separation of the numerous amino-acids resulting from the hydrolysis of the proteins constitutes a difficult problem, which has recently been solved by E. Fischer for the amino-acids and by Kossel for the diamino-acids. Fischer subjects the esters of the amino-acids to fractional distillation *in vacuo* and thus determines their separate amounts.

It is thought that the amino-acids occur in the proteins in a condensed form similar to **Glycylglycine**, $NH_2 \cdot CH_2 \cdot CO \cdot NH \cdot CH_2 \cdot CO_2H$. Indeed, Fischer was able to synthesise the so-called **Polypeptides**, which contain such groups and in many respects resemble the natural peptones derived from proteins (*see later*); the esters of the amino-acids readily give up alcohol and undergo ketonic condensation to polyanhydrides, and these, under the influence of alkali, take up a molecule of water, giving the peptides:

$$2NH_2 \cdot CH_2 \cdot CO_2C_2H_5 = 2C_2H_5 \cdot OH + NH{<}\begin{matrix}CO \cdot CH_2\\ CH_2 \cdot CO\end{matrix}{>}NH \text{ (and this} + H_2O)$$

Ethylglycocoll — Double Anhydride or Diketopiperazine

$$\rightarrow NH_2 \cdot CH_2 \cdot CO \cdot NH \cdot CH_2 \cdot CO_2H$$

Dipeptide or Glycylglycine

By chlorinating the carboxyl of the dipeptide with PCl_5 in acetyl chloride solution, a second molecule of ethylglycocoll may be caused to react with formation of a tripeptide, and so on, higher polypeptides similar to the natural ones being ultimately obtained,

$$X \cdots CO \cdot Cl + NH_2 \cdot CH_2 \cdot CO_2 \cdot C_2H_5 = HCl + X \cdots CO \cdot NH \cdot CH_2 \cdot CO_2 \cdot C_2H_5 \, ;$$

these polypeptides are completely hydrolysed by hot concentrated HCl, are digested by tryptase, withstand cold alkali, are soluble in water and insoluble in alcohol, and give the reactions of the proteins (*see below*). These syntheses, which represent the first small step towards the synthesis of the proteins, give an idea of the enormous difficulties to be overcome before the natural proteins can be reconstructed. Indeed, since the dipeptides have molecular weights of about 100, while with the proteins the molecular weight certainly exceeds 10,000, at least 100 of these groups must be present. Also, as several of the amino-acids contain one or more asymmetric carbon atoms, stereoisomerism is possible, and so likewise is tautomerism, *e.g.*,

$$\text{—HN} \cdot \text{CO—} \rightleftarrows \text{—N} : \text{C(OH)—}$$

The investigations of Fischer have resulted in the synthetical preparation of more than a hundred of the simpler polypeptides, and of a tetradecapeptide, but on ascending the series the complications and difficulties increase disproportionately. This problem could occupy a whole generation of chemists, and its solution would be a glorious triumph for the twentieth century, as it would banish for ever the Malthusian threat that one day humanity will be starved owing to the disproportion between the population and the productive capacity of the earth. Indeed, while it is not possible to replace the proteins in human nutriment by fats or carbohydrates—these alone leading to rapid decay of the organism and to death—proteins of themselves are able to supply all the needs of the organism. So that the insufficient production of proteins in nature at some future time would of a certainty be accompanied by famine, unless a method of synthesising proteins by chemical means had previously been discovered. Berthelot imagined that one day the air would supply the oxygen and nitrogen, and water the hydrogen for this synthesis, and it is not for us to deny that the dream of yesterday may become the reality of to-morrow, if chemistry learns how to imitate the simplicity and economy of the natural synthetical processes best exemplified in plants, which from carbon dioxide, water, and nitrates are able to effect continuous production of carbohydrates, fats, and proteins. Our laboratory synthetical methods are still too cumbersome, too indirect, and generally too costly. Only when the action of catalysts and light and the laws of colloids have been more closely studied can any hope be entertained of a more rapid progress in the synthesis of such complex organic substances.

The numerous different proteins are usually classified in the following groups and sub-groups:

I. NATURAL PROTEINS

(1) **ALBUMINS** (of eggs or Egg-albumin, of blood serum or *serum-albumin*, of milk or *lactalbumin*, of muscles, of plants, etc.).

These are the most common and also the best known of the proteins, since they can

be isolated as definite, crystalline, chemical individuals. They are soluble in water, dilute acid or alkali, or *neutral* solutions of NaCl, $MgSO_4$, or $(NH_4)_2SO_4$ (the globulins being insoluble), but in acid solution these salts precipitate the albumins. In the hot they are coagulated.

The products of the putrefaction of albumin contain also *p*-Hydroxyphenylacetic Acid, $OH \cdot C_6H_4 \cdot CH_2 \cdot CO_2H$, which occurs likewise in urine (acicular crystals coloured greenish by ferric chloride).

There exists nowadays a considerable trade in dry albumin obtained from the egg and from blood. In various countries, eggs and yolks are preserved in salt and employed in different industries (for tanning, making lecithin,[1] culinary purposes, etc.), and the fresh white separated is diluted with a little water, beaten until it forms a froth, allowed to stand until the latter is destroyed, filtered through woollen bags, and evaporated in a stream of air at 30° to 40° in large shallow pans; after 40 to 60 hours there remains a thin, yellowish, transparent pellicle, which is completely soluble in water and keeps without developing any unpleasant odour.[2]

[1] Lecithin, $C_{42}H_{86}O_9NP$ (*see* p. 462), is an ester of choline (p. 257) and of glycerophosphoric acid, combined as a glyceride of palmitic or stearic acid. When boiled with water or barium hydroxide it decomposes into choline, glycerophosphoric acid (p. 258), palmitic and stearic acids. Its constitution, first studied by Strecker (1868), would therefore be:

$$\begin{array}{l} CH_2—O \cdot CO \cdot C_{17}H_{35} \\ | \\ CH—O \cdot CO \cdot C_{15}H_{31} \\ | \\ CH_2 \cdot O \cdot PO(OH) \cdot O \cdot CH_2 \cdot CH_2 \cdot N(OH)(CH_3)_3. \end{array}$$

It is dextro-rotatory, but when heated with 95 per cent. alcohol is racemised to the inactive form, which is converted into *l-lecithin* by the action of lipase (p. 134). Distearic and dioleic lecithins are also known.

Lecithin occurs in the animal kingdom [nerves, brain, blood corpuscles, egg-yolk (9·4 per cent.)] and in the oils and seeds (0·5 to 2 per cent.) of cereals and leguminous plants. It forms an orange-yellow, waxy, crystalline mass, and is soluble in alcohol, ether, chloroform or glycerine, and slightly so in acetone or ethyl acetate. It is hygroscopic and with water swells and forms an opalescent solution, from which it is separated by various salts (including $PtCl_4$); it combines with both acids and bases, forming salts. Lecithin is decomposed by the pancreatic juice, the resulting products being completely resorbed by the intestine.

It is largely employed as a tonic, either as such or in the form of various salts. It intensifies metabolic processes, causes assimilation of phosphorus and nitrogen, reinvigorates the blood, and results in increase of weight.

Industrially lecithin is extracted from egg-yolk, in which it occurs partly combined with albumin as *lecithalbumin*, which may be isolated unchanged and then decomposed into its components by heating with alcohol. To obtain lecithin, 10 kilos of egg-yolk is shaken with 10 kilos of cold methyl alcohol (this dissolves less fat than ethyl alcohol) for three hours, left overnight and filtered, the residue being washed with 10 kilos of methyl alcohol in several portions. The alcohol is then distilled off under diminished pressure and the lecithin thus obtained dissolved in ether and reprecipitated with acetone.

According to Fr. Pat. 390,683, the fat and cholesterol are dissolved and the lecithalbumin left undissolved when egg-yolk is treated with ethyl acetate. Separation of lecithin as its salt with cadmium chloride is more complicated. Many other processes have been patented.

Before the war egg lecithin was sold at £3 to £4 per kilo, but during and after the war the price increased greatly.

[2] The *eggs* produced by hens of different breeds are of varying size and weight (from 45 to 65 grms.; duck, goose, and turkey eggs weigh from twice to four times as much) and are composed of about 60 per cent. of white, 30 per cent. of yolk, and 10 per cent. of shell (mainly calcium carbonate); the white contains 86 per cent. of water and 13 per cent. of albumin, and the yolk about 51·5 per cent. of water, 28·5 per cent. of fats, 15·8 per cent. of proteins (principally vitellin), 2 per cent. of salts, 0·45 per cent. of cholesterol, 1·2 per cent. of phosphoglyceric acid, and 0·4 per cent. of extractive substances. As regards its nutritive value, an egg weighing 60 grms. is equivalent to 50 grms. of meat, while its heat value is about 80 Calories. Continuous evaporation of water takes place through the shell of the egg, and the volume of the contents diminishes, leaving a free air-space—varying in size in different eggs—which may be observed by looking through the egg at a candle flame in a dark chamber. Fresh eggs are also distinguishable from stale ones by the specific gravity: fresh eggs sink in a salt solution of sp. gr. 1·078, those 2 to 3 weeks old in one of sp. gr. 1·060, those 3 to 5 weeks old in one of 1·050, and rotten eggs in one of sp. gr. 1·015. It has also been observed that fresh eggs float horizontally on a denser liquid, those 4 to 6 days old at an angle of 20°, those 8 to 10 days old at an angle of about 45°, and those 15 to 20 days old at an angle of 60°.

The *preservation of eggs* is of considerable importance, since in summer eggs are abundant and cheap, while in winter they are scarce and cost double as much. A common means of preservation formerly employed consisted in immersing the eggs in water saturated with lime (which partially filled up the pores of the shell with calcium carbonate), but in this way they

From fresh blood (from the butcher's) pure albumin is separated with greater difficulty. The blood is first allowed to undergo spontaneous coagulation, the blood globules and other impurities thus collecting in a compact mass so as to allow of the ready decantation of the faintly coloured liquid serum containing the albumin; or, after coagulation, the blood may be introduced immediately into a centrifugal separator (*see* p. 476). The centrifuged or decanted liquid is beaten (without dilution), filtered, decolorised with charcoal, and dried as above. In many cases decolorisation is difficult, and the albumin has to be precipitated with lead acetate; the decanted precipitate is washed and suspended in water, which is then saturated with carbon dioxide, the lead carbonate being allowed to settle. The clear albumin solution is treated with a little hydrogen sulphide, which removes traces of lead, and filtered, and the pure solution evaporated as with egg-albumin.

According to Ger. Pat. 143,042, the serum-albumin is coagulated by means of salt, dissolved in ammonia and treated at the boiling-point with hydrogen peroxide, the excess of ammonia being subsequently driven off. The method described in Eng. Pat. 10,227 (1905) consists in treating the serum successively with hydrosulphite, acetic acid, and sodium acetate, the liquid being then neutralised with ammonia and evaporated as usual.

Albumin is used in various industries: for photographic papers, in textile printing, in printing titles in gold-leaf on books, as a clarifying agent in wine-making (*see* p. 260), etc.

Egg-albumin cost, before the war, according to its degree of purity, £24 to £28 per quintal. Blackish blood-albumin was sold at 48*s*. to 60*s*. per quintal, the dark at 88*s*., the pale at £5 to £8, and the pale powdered at 128*s*. to 208*s*.

(2) **GLOBULINS** (of plants or **Phytoglobulins, Serum-globulin, Lactoglobulin,** etc.) are insoluble in water but soluble in dilute acid or alkali. At 30° they are precipitated unchanged completely by solutions of ammonium or magnesium sulphate and partly by sodium chloride solution. Their solutions are coagulated by heat.

(3) **NUCLEO-ALBUMINS (Vitellin, Casein,** etc.) are acid in character and decompose carbonates; they are slightly soluble in water, but dissolve with formation of salts in caustic soda or ammonia and are then coagulated neither by heat nor by alcohol. They contain phosphorus (0·85 per cent. in casein) but are distinct from the nucleo-proteins, which give xanthine bases among their decomposition products. **Casein** is found in milk (*see* p. 643) and is coagulated by rennet or by dilute acids at 50°; it is soluble in borax or potassium carbonate and is rendered insoluble by formaldehyde. Converted into salts in various ways, it is placed on the market as a concentrated and readily digestible food (*plasmon, nutrose, tropon*, etc.); it is mixed with mineral colouring-matters to make varnishes. The hydrolysis of casein yields various amino-acids and complex tribasic acids (Skraup). *Vegetable caseins* are also known.

To obtain pure casein in the laboratory, diluted skim-milk to which 0·5 per cent. of acetic acid has been added is heated to 55° to 60° and the precipitated casein collected on cloth, washed well with water, redissolved in very dilute ammonia, decanted or filtered to remove the undissolved fat and nuclein and then reprecipitated with acetic acid as at first. It is again collected on cloth, washed with alcohol and then with ether, and dried in a vacuum. Prepared in this way, it is free from fat, leaves less than 0·5 per cent. of ash and contains 15·5 to 18 per cent. of nitrogen. From ordinary casein a modification known as *paracasein*, containing 14·8 to 15 per cent. of nitrogen, may apparently be separated. Commercial casein (*see* p. 643) contains less than 3 per cent. of ash and less than 0·1 per cent. of fat, and costs 64*s*. to 80*s*. per quintal. Riegel (Ger. Pat. 117,979 of 1900) precipitates it in a highly pure state from milk by means of ethylsulphuric acid. Casein is detected on textiles or paper by Adamkiewicz's reaction, a drop of a mixture of glyoxylic and sulphuric acids

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acquire an unpleasant taste; an improvement is effected by adding 5 per cent. of sodium chloride to the lime water. Others preserve them in pounded salt or in salt and bran, pointed end down, while others again smear them with wax, vaseline, and oil or tallow. Large quantities of eggs are now preserved for some months (May to November) by placing them in thin layers on wooden lattices in cold chambers, which are kept at a temperature of 1° to 2° and a humidity of 70° to 80°, and are well ventilated, preferably by means of an apparatus producing ozonised air. In certain cases good results are obtained by preserving the eggs in 10 per cent. sodium silicate solution, although such eggs often burst during subsequent boiling. A mere coating of the silicate or of collodion is of little avail. For transport eggs are arranged in layers, with alternate layers of old straw, in wooden boxes.

The value of the eggs imported into England was £80,000 in 1864, £8,000,000 in 1906, and £6,800,000 in 1910 (about £3,300,000 from Russia, £1,750,000 from Denmark, £560,000 from Austria-Hungary, £420,000 from France, £360,000 from Italy, £200,000 from Germany), in addition to £3,800,000 from Ireland.

being placed on the surface, which is then gently heated over a flame: in presence of casein, the drop of liquid assumes a transitory violet-red colour.

(4) PROTEINS WHICH COAGULATE (Fibrinogen, Myosin, etc.) are distinguished by exhibiting a first coagulation under the influence of certain enzymes and a further coagulation by heat or absolute alcohol.

(5) HISTONES (Globin, Nucleo-histone, etc.) contain sulphur and are markedly basic in character; they are precipitated by alkalis, and in acid solution give insoluble compounds with the albumins. *Nucleo-histones* are obtained from the leucocytes of the thymus gland and from the testes of certain fish. The protein part of the hæmoglobin molecule of the red blood corpuscles consists of a histone, *globin*. The histones have certain properties in common with the peptones and albumoses.

(6) PROTAMINES (Salmin, Clupein, Sturin, etc.) do not contain sulphur but contain up to 25 per cent. of nitrogen and are composed mainly of diamino-acids (arginine); they are obtained from the spermatazoa of many fishes (salmon, herring, sturgeon, etc.). They and the histones are the least complex proteins.

They are still more basic in character than the histones and readily form platinichlorides, sulphates, and picrates, which are all crystalline. They are precipitated by dilute alkalis.

II. MODIFIED PROTEINS

(1) ALBUMOSES and PEPTONES are derived from true proteins by various transformations. The albumoses are soluble and cannot be coagulated, but are precipitable by ammonium sulphate and other salts. The peptones are regarded as the last decomposition products of the proteins which give protein reactions (the biuret reaction); on decomposition they give amino-acids without intermediate products.

(2) SALTS OF PROTEINS (Syntonins or Acid-albumins, Albuminates) are markedly acid in character.

III. CONJUGATED PROTEINS (PROTEIDS)

These represent combinations of proteins with other complex substances, and are coagulable by alcohol.

(1) HÆMOGLOBIN is the colouring-matter of red blood corpuscles and is regarded as a protein combined with a colouring-matter containing iron, since, when defibrinated blood is heated on a water-bath with sodium chloride and acetic acid, the hæmaglobin is decomposed into albumin and Hæmatin, $C_{33}H_{32}O_4N_4Fe\cdot OH$. The latter is a brown substance containing 8 per cent. of iron, and by treatment with sodium chloride is transformed into Hæmin, $C_{33}H_{32}O_4N_4Fe\cdot Cl$, which forms characteristic, reddish brown, acicular crystals. The constitution of hæmatin has been elucidated by the work of Nencki and Zaleski (1901), Küster (1901, 1906, 1914), Willstätter, Knorr, Piloty, and H. Fischer (1911, 1912), and that of the hæmatinic or hæmatiniminic acid obtained on oxidation renders certain the presence of the pyrrole complex, $NH\!\left<\begin{matrix} CO\cdot C\cdot CH_2\cdot CH_2\cdot CO_2H, \\ \| \\ CO\cdot C\cdot CH_3 \end{matrix}\right.$ this yielding succinic acid when oxidised with bichromate or permanganate. The hæmoglobin of venous blood is of considerable importance in respiration, as it combines very readily with atmospheric oxygen (when the blood traverses the lungs) forming **Oxyhæmoglobin,** which is found in arterial blood and carries the oxygen to the tissues, afterwards returning to the veins. **Blood-spots** (even old ones) may be detected by Teichmann's test: to a solution of the spot in a little glacial acetic acid are added a trace of sodium chloride and then a small quantity of pure concentrated acetic acid, the liquid being heated to boiling on a watch-glass and one or two drops of the hot solution placed on a microscope slide and allowed to evaporate slowly in the cold; a drop of water is added, a cover-glass applied, and the slide observed under the microscope. The brown hæmin crystals resemble barley-corns, but are sometimes rhombohedral and generally crossed in groups (Fig. 556); viewed in polarised light between crossed nicols, they appear luminous and golden on a dark ground. They are insoluble in water or cold acetic acid, but dissolve in alkali.

Blood-stains may also be identified by means of the catalytic action of the hæmoglobin,

which colours alcoholic guaiacol tincture or alkaline phenolphthalein previously decolorised by zinc dust or, better, the leuco-base of malachite green (F. Michel, 1911).[1]

T. Gigli (1910) states that a very sensitive reaction is given by a fresh mixture of 3 drops of benzidine (5 per cent. solution in acetic acid) and 2 drops of 3 per cent. hydrogen peroxide solution; a blue coloration is given immediately by a trace of blood. Bardach and Silberstein (1910) propose the use of guaiacum resin and sodium perborate.

Oxyhæmoglobin has a composition differing little from that of the proteins, but it contains 0·4 per cent. of iron combined in the ferric state, as with hæmin and hæmatin, whilst the reduction product of the latter, *i.e.*, hæmoglobin, is a ferrous compound (W. Küster, 1910). In a vacuum (or under the action of ammonium sulphide) it loses oxygen giving hæmoglobin.

Hæmoglobin forms a red crystalline powder soluble in water and reprecipitable in the crystalline state by alcohol. Both hæmoglobin and oxyhæmoglobin give characteristic absorption spectra.

Hæmoglobin and also its ash exert a catalytic action in certain combustion phenomena; *e.g.*, sugar moistened with a little human blood burns with great energy.

When a current of carbonic oxide is passed into a solution of red oxyhæmoglobin (defibrinated blood) the oxygen is displaced and the liquid assumes a violet-red colour, *carboxyhæmoglobin*—which can be obtained in bluish crystals —being formed. An aqueous solution of this compound (blood poisoned with carbonic oxide) gives two characteristic absorption bands between the D and E lines of the spectrum, and these bands do not unite or disappear—as happens in the case of oxyhæmoglobin—when a few drops of ammonium sulphide are added to the solution. Hæmoglobin itself gives a single absorption band between the D and E lines.

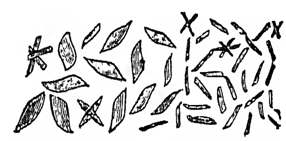

FIG. 556.—Hæmin crystals at different magnifications.

(2) **NUCLEOPROTEINS** or **Nucleins** have a pronounced acid character and are insoluble in water and acids, but soluble in alkali. They represent compounds of proteins with a **Nucleic Acid**, which is phosphoric acid neutralised partially by basic organic groups, such as xanthine, guanine, etc. The nucleins contain 5·7 per cent. P, 41 per cent. C, and 31 per cent. O, and are hence sharply distinguished from true proteins although they give the same colour reactions. They form the fundamental constituents of cell nuclei.

(3) **GLUCOPROTEINS** are acid in character and are formed of a protein combined with a sugar derivative. They are insoluble in water and with a little lime-water give neutral, frothy, and ropy solutions which are not coagulated by heat or by nitric acid. When hydrolysed with alkali or acid they yield sugar, peptones, and **Syntonins**.

These compounds, which are poor in nitrogen (11·7 to 12·3 per cent.), include the **Mucins**.

IV. ALBUMINOIDS

These constitute the fundamental parts of the cartilaginous tissues and epidermis of animals and comprise:

[1] **Blood-spots** may also be detected by means of hydrogen peroxide: it is sometimes sufficient to press a piece of moistened filter-paper on the dry blood-spot and then to immerse it in hydrogen peroxide solution, to obtain a copious evolution of oxygen.

To ascertain from what animal the blood comes, and in general to discover if it is human blood, Uhlenhuth's test (1909), based on the formation of different antitoxins in different animals (*see* p. 138), serves. Tristovitch and Bordet (1899) showed, indeed, that if an extraneous serum (*e.g.*, human) is injected in several doses into the blood of an animal (*e.g.*, a guinea-pig), the serum of this animal (*antiserum*) ultimately acquires the property of precipitating (or rendering turbid in the case of dilute serum or dilute blood) the blood of the animal which furnished the injected serum (*e.g.*, man). If even a very dilute solution of blood (obtained, for instance, by extracting a dried blood-spot with a little water) is cleared by filtration and treated separately with different clear antisera to ascertain with which of them a turbidity is produced, it can be stated with certainty that the blood-spot was derived from the animal whose serum, when injected into the guinea-pig, produced the antiserum rendering the blood solution turbid. The test must be applied very carefully and with parallel control experiments; it does not distinguish between the bloods of similar animals, *e.g.*, hens and pigeons, sheep and goats, apes and men. The difference between various species becomes more evident when dilute solutions or, better, dilute blood and a little concentrated antiserum are employed. All these phenomena, studied by Uhlenhuth, and subsequently by others, are based on the precipitation of the albuminoid substances of the different sera (*precipitins*), and they allow of the determination of the character of blood-spots 60 years old. Clear solutions and sterilised vessels are always used for the test.

(1) **ELASTIN**, which forms the elastic part of the tendons and ligaments, is insoluble in dilute acid or alkali, but with the latter loses the whole of its sulphur.

(2) **KERATIN** is the principal constituent of the nails, horns, feathers, epidermis, hair, etc. It is insoluble in water, but when heated under pressure, best in presence of alkali, it dissolves with partial decomposition. It contains 4·5 per cent. of sulphur, which is eliminated to some extent by boiling water.

With nitric acid it gives the yellow xanthoprotein reaction (*see above*, yellow spots on skin treated with nitric acid).

(3) The **COLLAGENS** are abundant in bones, hair, tendons, and cartilage. They combine with water at the boiling-point and dissolve, forming ordinary *glue* or *gelatine*, which is precipitated by tannin or by mercuric chloride acidified with HCl but not by mineral acids. They contain stably combined sulphur. They consist, to the extent of 85 per cent., of amino-acids (Skraup, Biehler and Böttcher, 1909–1910), and, like the protamines, are true proteins containing methoxy- and azomethyl-groups. Unlike casein, they give little glutamic acid on hydrolysis. On hydrolysing them with caustic baryta, E. Fischer and R. Boehner (1910) obtained **Proline** (*pyrrolidine-α-carboxylic acid*) as primary product; **α-Amino-δ-hydroxyvaleric Acid**, which is also obtained from gelatine, does not give proline with baryta. By digesting gelatine with trypsin, Levene (1910) obtained mainly **Prolylglycocoll Anhydride**. The absorptive power of the collagens for carbon disulphide, which in presence of alkali leads to thiohydration, allows of their differentiation from agglutinating substances (Sadikow, 1910); the agglutination of gelatine is not only a disgregation of the collagen molecule, but also a condensation of the side-chains. Gelatine which has undergone prolonged exposure to light loses some of its absorptive power for water owing to the formation of formaldehyde, which hardens the glue (Meisling, 1909). On hydrolytic decomposition, the collagens give glycocoll (while the albumins give tyrosine, leucine, glutamic acid, and asparagine.[1] Very dilute solutions of glue give, with boiling

[1] **Manufacture of Glue and Gelatine.** The prime materials are bones and hide waste, generally untanned and preserved with lime. From bones the fat is first extracted (*see* p. 486 and also Vol. I., p. 647), and the crushed bones then heated for a couple of hours in a large autoclave with water and steam under pressure, so as to convert the *ossein* into soluble gelatine; this treatment is repeated two or three times, the final more dilute solutions being used for a subsequent operation. Batteries of autoclaves are generally used. The solution obtained shows 12° to 14° on the glue-densimeter and is concentrated in a vacuum (*e.g.*, in a Kestner apparatus, Vol. I., p. 563) to 45° to 46°, and then discharged into zinc moulds surrounded by cold water to solidify. In some cases, however, the bones and hence also the glue are freed from calcium phosphate by treatment with four times their weight of 6 to 7 per cent. hydrochloric acid (sp. gr. 1·05) until complete softening occurs. The calcium phosphate is precipitated from the solution by means of lime and calcium carbonate, while the ossein, placed in a double-bottomed vessel heated by steam, is rapidly converted into a solution of glue. According to Ger. Pat. 144,398, the calcium phosphate may be dissolved by aqueous SO_2 *under pressure* (only the treatment under pressure is patented). The solid blocks of glue are then cut into suitable sizes and dried on wide-meshed nets arranged on trolleys, which are placed in chambers through which air at 25° to 30° is circulated by means of fans. If the air is above this temperature the glue will melt, while if it is too dry the cakes are deformed. On this account, and also because it would readily putrefy, glue is not made in summer. Dry *bone-glue* contains 15 to 20 per cent. of water, the drying occupying 10 to 12 days. When the mineral part of the bones is dissolved by SO_2 or a mineral acid, *gelatine* remains.

Skin-glue (leather glue) is prepared from hide-waste and also other waste (nerves, cartilage, etc.) by defatting with carbon disulphide and softening or swelling in water, which likewise removes impurities. It is then macerated for three weeks in a series of vessels containing milk of lime, which is frequently renewed to eliminate any remaining fat, blood, etc. It is then thoroughly washed in water and the last traces of lime (which would make the glue turbid) removed by means of dilute hydrochloric acid, or, better, of sulphur dioxide or phosphoric acid. The waste prepared in this way is treated with hot water and steam in wooden vessels with false bottoms. and the first solutions, showing densities of 16° to 20° on the glue-densimeter, are solidified in moulds as above. The two or three succeeding extracts, which are more dilute, are concentrated to 20° to 22° in a single or multiple-effet vacuum apparatus (*see* p. 560), surmounted by a column with perforated discs to break up the froth, and are then allowed to set. Good results are now obtained with Kestner concentrators (*see above*). The waste used gives about one-third of its weight of dry glue. The finer qualities, filtered, decolorised, and prepared from pure, fresh, raw materials, bear the name of *gelatine* and cost almost double.

In order to utilise tanned hides in the manufacture of glue it is necessary to untan them by successive treatments with dilute alkali solution, water, and lime; if chrome tanned, they are treated first with dilute sulphuric acid, then with an abundant supply of water and finally with lime. In either case, the remaining traces of lime are removed by means of dilute HCl, the latter being eliminated by treatment with alkali and washing with water (Eng. Pat. 22,738 of 1902).

Fish-glue is obtained from the well-purified swimming-bladders of various species of *Acipenser*,

ammonium molybdate solutions, a characteristic precipitate and coloured solution, which may be applied to quantitative estimations (E. Schmidt, 1910).

V. VARIOUS PROTEINS

Spongin enters into the formation of sponges; its hydrolytic products approximate more to those of the collagens than to those of the albumins, but they are more resistant to the action of soda and baryta than collagens. **Cornein** constitutes coral and gives leucine on hydrolysis. **Fibroin** and **Sericin** are obtained from silk (*see* p. 813); fibroin dissolves in energetic alkalis with elimination of ammonia and formation of **Sericoin**, and when completely hydrolysed it yields tyrosine and glycocoll but not leucine.

The **Enzymes** (*see* p. 134) belong to the group of complex albumins.

GLUCOSIDES AND OTHER SUBSTANCES OF UNCERTAIN OR UNKNOWN COMPOSITION

Glucosides have been defined and the synthesis of artificial glucosides described on pp. 530 and 531. They are compounds of aromatic or aliphatic compounds with carbohydrates. In vegetable organisms these glucosides form, according to Pfeffer, difficultly dialysable substances which serve the plants as reserve material, gradually becoming utilisable as they are decomposed by the various enzymes occurring in other cells. This was well shown by T. Weevers (1903 and 1908) for **Salicin**, which is decomposed (by emulsin) into glucose and saligenin (hydroxybenzyl alcohol), the latter being probably further transformed into a final product known as **Catechol**. The latter is a phenol found throughout the whole plant (*e.g.*, *Salix purpurea*), and its quantity is inversely proportional to that of the salicin present; it is possible that it reacts with fresh quantities of glucose, regenerating salicin. Whilst the sugars are gradually utilised in the growth of the plant, the aromatic group (which serves as a reserve of carbon for bacteria but not for yeasts) is used in the continuous reconstruction of the glucoside. Thus plants are able to prepare reserve materials in different ways: when the carbohydrates are not utilised, they are transformed into insoluble starch, or into glycogen, or into glucosides.

AMYGDALIN, already mentioned on p. 136, has a composition corresponding with $C_{20}H_{27}O_{11}N$ and forms colourless crystals which are soluble in water and melt at 200°. It is found in the stones of various fruits (cherries, peaches, bitter almonds, etc.) and in the leaves of the cherry-laurel. When hydrolysed by acids or enzymes (*see* p. 134) it yields dextrose, prussic acid, and benzaldehyde.

SAPONIN, $C_{32}H_{52}O_{17}$, is obtained from Saponaria root, quilaya bark, and the Indian chestnut. It is used for washing garments in place of soap, and is also employed to produce a persistent froth (*e.g.*, to give a head to beer). It is soluble in water, has an irritating taste and smell, and dissolves red blood corpuscles (is hence poisonous). It is extracted

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especially of *Acipenser sturio* (sturgeon), by treatment with acid, lime, steam, water, etc. According to Ger. Pat. 131,315, the blubber of whales may also be used. Fish-glue costs double or treble as much as the best qualities of other glue.

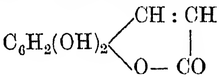
Liquid glue is obtained by the protracted heating of glue with its own weight of water and one-fourth or one-third of its weight of hydrochloric, acetic, or nitric acid (the last at 35° Bé.; the nitrous fumes must be carried away by a good draught). F. Supf (Ger. Pat. 212,346 of 1908) obtains liquid glue by treating, say, 450 kilos of glue with 120 kilos of sodium naphthalene-sulphonate.

Glue is *analysed* by determining the ash (2 to 3 per cent.) and the increase in weight caused by immersion for 12 hours in cold water (in which it should not dissolve), the best qualities absorbing most water and swelling. The ash of bone-glue has an almost neutral reaction, and chlorides and phosphates are found in its nitric acid solution. The ash of hide-glue does not melt, has an alkaline reaction, and contains little or no phosphoric acid. The aqueous solution of pure glue has a neutral or very faintly acid reaction, while those of the more impure kinds are sometimes alkaline. Glue should be completely soluble in hot water, any undissolved part representing impurity. The moisture content of dry glue should not exceed 15 to 18 per cent. (lost at 105°). The best qualities melt at the highest temperatures and the dropping-point may be determined by Ubbelohde's apparatus (*see* p. 6), using a larger vessel. The relative adhesive powers of different glues may be estimated by preparing tepid solutions of equal concentrations, immersing pieces of cotton or woollen fabric (of equal weights and areas) in them for 2 or 3 minutes, centrifuging the fabrics at the same time in the same centrifuge, ironing them slightly with a hot iron, drying completely in an oven at 100° and then noting which of the fabrics adheres best and longest to the fingers.

in various ways according to Ger. Pats. 116,591, 144,760, and 156,954. The crude product cost, before the war, 9*s.* 6*d.* per kilo ; the purified, 20*s.*, and the puriss., 40*s.*

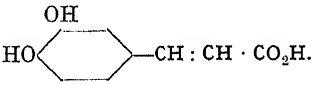
DIGITALIN, $C_{35}H_{56}O_{14}$ (?); **DIGITONIN**, $C_{27}H_{46}O_{14}$, and **DIGITOXIN**, $C_{31}H_{54}O_{11}$, are the most important constituents of the foxglove (*Digitalis purpurea*) and are used in medicine, especially for diseases of the heart. Pure digitalin cost, before the war, 10*d.* per gram, and crystallised digitoxin 20*s.* per gram.

SALICIN, $C_{13}H_{18}O_7$ (*see* pp. 535, 677), is contained in several varieties of Salix, and on hydrolysis gives glucose and saligenin (*see* pp. 641, 677); with nitrous acid it forms **Helicin**, $C_{13}H_{16}O_7 + H_2O$, which can also be obtained synthetically from glucose and salicylic aldehyde.

ÆSCULIN, $C_{15}H_{16}O_9$, is obtained from horse-chestnut bark, and is the glucoside of **ÆSCULETIN** (a **Dihydroxycoumarin**), , which is isomeric with *daphnetin.*

POPULIN, $C_{20}H_{22}O_8 + 2H_2O$, is a **Benzoylsalicin**, and is obtained synthetically from salicin and benzoyl chloride ; it occurs naturally in *Populus.*

HESPERIDIN, $C_{22}H_{26}O_{12}$, occurs abundantly in the bitter orange, and on decomposition gives phloroglucinol, glucose, and **Ferulic Acid**, which is the monomethyl ether of

Caffeic Acid, 

PHLORETIN, $C_{15}H_{14}O_5$, and its glucoside, **PHLORIDZIN**, $C_{21}H_{24}O_{10}$, are found in plants, and in cases of glycosuria in animals.

IRIDIN, $C_{24}H_{26}O_{13}$, is found in the roots of the Florentine iris and yields **Irigenin** and glucose on hydrolysis.

ARBUTIN, $C_{12}H_{16}O_7$, occurs in the leaves of the bear-berry and gives glucose and hydroquinone on hydrolysis. **Methylarbutin** gives glucose and methylhydroquinone.

CONIFERIN, $C_{16}H_{22}O_8 + 2H_2O$ (*see* p. 678).

SINIGRIN (**Myronic Acid**), $C_{10}H_{17}O_9NS_2$; hydrolysis of its potassium salt, which occurs in black mustard seed, gives glucose, potassium bisulphate, and allyl mustard oil.

SANTONIN, $C_{15}H_{18}O_3$; its constitution has been studied more especially by Cannizzaro and his pupils. It is a naphthalene derivative and is found in worm-seed (santonica).

ALOIN, $C_{17}H_{18}O_7$, an anthracene derivative, occurs in aloes and is a strong purgative.

LECITHIN (composition, *see* pp. 462, 860) is a characteristic component of egg-yolk and of brain and nerve matter and is a crystalline waxy substance, which dissolves in alcohol or ether and with water forms an opalescent liquid. When hydrolysed it yields glycerophosphoric, oleic, and palmitic acids, together with choline, and it may therefore be regarded as a glyceride (*see* pp. 218, 460).

Considerable use has been made of it (and also of bromo- and iodo-lecithin) in recent years as a medicine. Lecithin is extracted on the large scale from egg-yolk, and new processes are described in Fr. Pats. 371,391 and 406,634 of 1908. Pure lecithin costs up to £8 per kilo.

CEREBRIN, $C_{17}H_{33}O_3N$, occurs in the nerves.

IODOTHYRIN (*see* Vol. I., p. 162) is the iodine compound of the thyroid gland.

Bile Compounds include **TAUROCHOLIC ACID**, $C_{26}H_{45}O_7NS$, and **GLYCOCHOLIC ACID**, $C_{26}H_{43}O_6N$, as sodium salts. When decomposed by alkali, both acids yield **Cholic Acid**, $OH \cdot C_{21}H_{32}(CH_2 \cdot OH)_2(CO_2H)$, glycine and taurine. Bile also contains colouring-matters such as **BILIVERDIN**, **BILIFUCHSIN**, and **BILIRUBIN**, $C_{16}H_{18}O_4N_2$.

CANTHARIDIN, $C_{10}H_{12}O_4$, occurring in cantharides, causes blistering of the skin, and sublimes in thin scales.

CHITIN forms the skeletal matter of crustaceans. It is insoluble in alkali (unlike keratin) and when hydrolysed by acid gives a glucosamine. Fusion with potash at 184° yields acetic acid and **Chitosan**, which also forms the glucosamine with acid.

CHOLESTEROL, $C_{27}H_{46}O$, occurs in many plants and animals (that of plants is called **Phytosterol**), generally together with fats and oils ; certain physical differences but virtually no differences in chemical behaviour are observable in products of different origin. Its constitution has not been definitely established, but, owing more especially to the investigations of A. Windaus, many of its component groups have been ascertained. A doubt

whether the complex contained one or two double linkings formerly existed, but the addition of ozone (Molinari and Fenaroli, 1908) shows the presence of two such linkings in both phytosterols and other cholesterols.

It forms shining scales melting at 147°, and in constitution it resembles the terpenes more than the substances of any other group, but in all probability it does not contain benzene groups. Minimal quantities of cholesterol may be detected by Tschugajew's reaction, which consists in the formation of a more or less intense red coloration when a small quantity of a substance containing cholesterol is poured into fused anhydrous trichloroacetic acid. In alcoholic solution, cholesterol and phytosterol (but not their ethers) form an insoluble compound with **Digitonin**; this reaction serves for the estimation of these substances and for their separation from other animal and vegetable organic compounds, such as hydrocarbons, etc.

VITAMINS.[1] The constitution of these compounds has not yet been determined, but they appear to be alkaloidal in character and to contain heterocyclic closed chain groupings. They are obtained from various animal glands, from seeds and bran and from beer yeast (which derives it from the malt) by extraction with alcohol slightly acidified with hydrochloric acid, the extract being concentrated in a vacuum, taken up with hot water and precipitated with phosphotungstic acid. The precipitate is treated with barium hydroxide, and the filtrate concentrated, dissolved in alcohol and precipitated by means of mercuric chloride. Precipitation of the filtrate with silver nitrate then yields a crystallised base melting at 233°, which may be resolved by repeated crystallisation into three other bases of different melting-points. The mixture of the three bases is the most active, and in two or three hours cures pigeons affected with polyneuritis. This mixture, analysis of which indicates the formula, $C_{26}H_{20}O_9N_4$, is soluble in alcohol or water, resists the action of dilute sulphuric acid (even 10 per cent.), dialyses easily, is sensitive to heat (90° or, rarely, 120°) or alkali, is absorbed by charcoal and by certain precipitated alumina (in preparing vitamins, these are separated from the liquids by centrifugation and not by filtration). With phosphotungstic or phosphomolybdic acid, crude vitamins give the reactions of uric acid. They do not usually occur free in nature, but are liberated on hydrolysis (even with 10 per cent. sulphuric acid) in an active condition. Gaglio found that human urine contains a vitamin which rapidly cures polyneuritis in pigeons.

When hydrolysed, both Funk's vitamin and the oryzanin separated from rice husks by Suzuki, Shimamura and Odake yield choline, glucose and nicotinic acid. Also Drummond and Funk showed that vitamins are pyridine derivatives. In some cases, *e.g.*, with hydrogen peroxide, they act as catalysts.

Mammals are incapable of producing vitamins and those present in the milk are derived from the food. Vitamins in excess are harmless to the human organism. Bottomley and Mockeridge gave the name *auximones* or *oximones* to species of vitamin which are produced during the fermentation of peat and facilitate the development of the nitrogen bacteria of the soil.

The study of vitamins is still in its infancy and many points connected with them remain controversial.

[1] C. Funk gave the name vitamin to a substance which may be extracted from rice bran and beer yeast and is capable of curing the disease known as beri-beri. In Java in 1896 Eijkman found that 28 per cent. of the prisoners fed on decorticated (polished) rice suffered from this disease, whereas the proportion was only 0·01 per cent. among those fed with whole rice (*see* p. 595). A similar phenomenon occurs with fowls, pigeons and rats, which are cured by simple administration of either whole rice or its bran. In 1910 Bréaudat and also Stepp confirmed Eijkman's results and showed that vitamins and lipoids (*see* p. 746) are not identical. McCollum and Davis (1915) maintained that, for regular and equilibrated growth of the animal organism, the food must contain two special substances which they term *factor A*, or *antixerophthalmic vitamin* (soluble in fats, but hydrolysable only with difficulty), and *factor B* (insoluble in fats, but soluble in alcohol or water). The latter corresponds with Funk's vitamin and occurs more or less abundantly in animal and vegetable foodstuffs; it abounds in milk and its products, egg-yolk, wheat, beans and soja beans, being localised especially in the cuticle or husk of seeds and in the embryo, but lacking in the starch.

Want of factor A (normally found in the lipoids of the glandular tissues, *e.g.*, the testicles, ovary, liver, etc., and in the leaves of cauliflower, clover, etc.) produces in adults *xerophthalmia*, and in the young *rickets*.

Scurvy is due to lack or deficiency of a specific vitamin occurring largely in fresh or germinating vegetables and in lemon or orange juice (it decomposes on drying at 90° to 100°). Funk obtained an *anti-scorbutic vitamin* which protects man from scurvy and beri-beri, and an *anti-beri-beri vitamin*; the latter is possibly formed by scission of the former (less stable), and abounds in oats, wheat and yeast and protects the organism from beri-beri, but not from scurvy, which is, indeed, the more common. Moist oats (wheat, peas) are anti-beri-beric, and on germination become anti-scorbutic. The relation of vitamins to pellagra is still very uncertain.

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